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Shale gas and "Snake oil"

"Geological characteristics of continuous petroleum resources and resource abundance evaluation assessment methodology for shale gas/oil in some European countries"

Department of Biotechnology, Chemistry and Environmental Engineering, Section of Chemical Engineering

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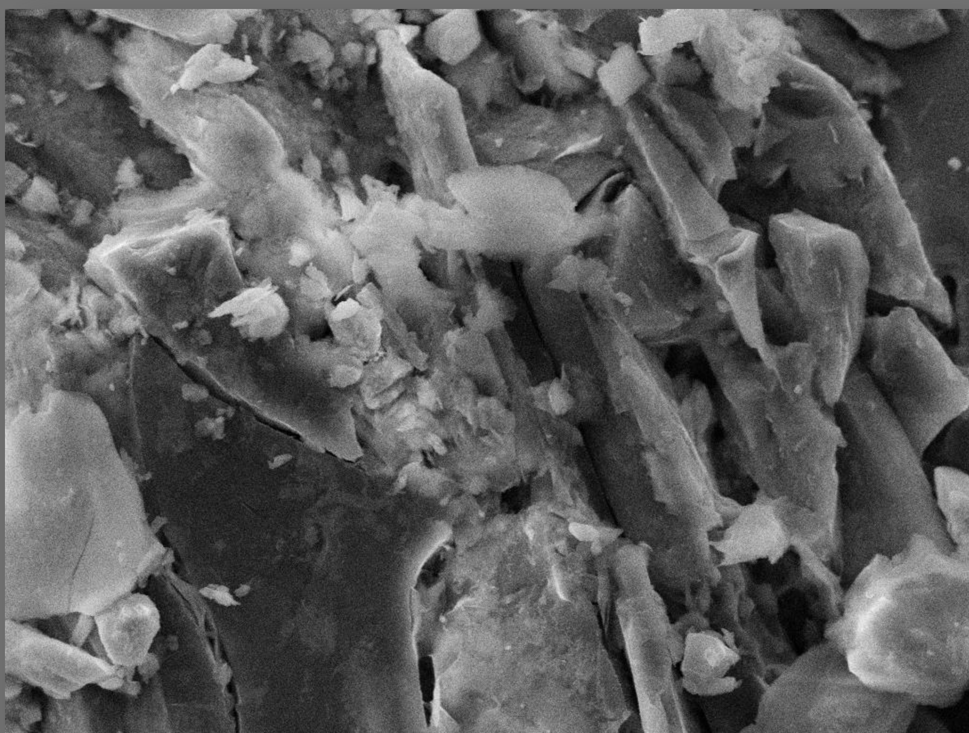

Supervisors:

Kim H. Esbensen

Niels H. Schovsbo

Author:

Kristiyan Nikolov

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University:

Aalborg University, Esbjerg University of Technology - Niels Bohrs Vej 8, 6700 Esbjerg, Denmark (www.en.aau.dk)

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Issued and presented by:

Kristiyan V. Nikolov – MsC Student in Faculty of Engineering and Science, Department of Biotechnology, Chemistry and Environmental Engineering

Phone: (+45) 52821968 / Email: knikol12@student.aau.dk / Employee No 20121290 /

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Supervisors:

1. Kim H. Esbensen

Geological Survey of Denmark and Greenland (GEUS)

Ø. Voldgade 10, DK-1350 Copenhagen K. Denmark (Room 01-121)

Phone +45 3814 2728 - ke@geus.dk

Professor, ACABS research group - Aalborg University Esbjerg Denmark

2. Niels H. Schovsbo

Senior researcher in Geological Survey of Denmark and Greenland (GEUS)

Ø. Voldgade 10, DK-1350 Copenhagen K. Denmark

Cell phone: +45 91333759 - nsc@geus.dk

Signature: K.Nikolov

[1]*Front Page Embedded Image – Interpores system in siltstone/mudstone rock sample (Sample BG1-J1), derived from SEM image with scale image magnification to 100 nm. (Own study investigation – Aalborg University Esbjerg)*

ABSTRACT AND SYNOPSIS

The extraction of continuous petroleum resource in North America, shale gas and oil in particular, in the last decade led to a growing attention on the prospective and risks during unconventional hydrocarbon extraction and production, also including Europe. The shale gas revolutions in the United States, stands as prove for the experience in the exploration of such resources. Furthermore, the harvesting of such unconventional fuels showed that shale gas could increase security of supply, or diversifying the energy sector. The experience of the U.S. also confirmed that intensive production of shale gas and oil entails environmental risks, caused by the ubiquitous use of horizontal drilling and hydraulic fracturing.

The master thesis conducted in the 9th and 10th semester of the Oil and Gas technology study in Aalborg University Esbjerg, tends to approach the large-scale exploration activities in some European countries, and serve as a handbook of resource potential for Denmark and Bulgaria in particular. Composed of relevant and up-to-date information and estimation numbers, its purpose is to synthesize the wide-scale of assessment methodologies and approaches for shale gas and oil resource potential estimation, discuss the relevance and trustworthy reservoir parameters and engineering formulas used in the methods, and modify evaluation procedure for more rigorous numerical outcomes in the shale gas potential calculations in Denmark.

The overall goal of this pilot study is to acquire an independent, scientific based, evaluation assessment of the resources in the Baltic Basin (Danish Alum Shale) and in some geological levels of the Bulgarian part of the Moesian Platform (Lower Carboniferous) by combining the knowledge from each survey, and the newly conducted experiments for the latter. Hopefully, this will result in improvement of assessments towards more rigorous approach, and less deviation from realistic shale resource in-place.

During the chapters, the discussion will be on the geological properties of shale, shale gas-bearing formations, investigation methods applied for evaluation of the resource base, the typical cases of the US experience with an emphasize on the Danish and Bulgarian unconventional oil and gas potential. By evaluating the potential of shale gas in Europe, this paper would infer to defining the risks of producing such fuels, and seeks to anticipate the challenges ahead of shale gas and oil extraction on the continent.

Because of the problematic nature of continuous petroleum resources, the confounding geological characteristics and difference between the conventional and unconventional resources, a comprehensive clarification to those terms will be given in the **Theory and Introductory part**. A full description of the new "*nano-hydrocarbon*" exploration, low-permeable reservoir characteristics, methods for identification of fine-grained sedimentary rocks, types of pores in shale, matrix permeability, adsorption and free gaseous state in shale reservoirs are presented in **Chapter I**. Socio-economical status of shale gas is also from great importance for triggering the flows in Europe, thus technologies used for extraction, their cost and profitability, stages in exploration and production of shale gas, and examples of best-case scenarios are provided in **Chapter I**. Last, but not least in the chapter, an insight of the concept of shale gas and "Snake oil", which is the corresponding title of the thesis report, explained concisely. The tag of the term in the report should be approached seriously with individual perceptions towards the problem, and should not be disregarded.

Chapter II deals with the screening and description of existing methods for calculation of unconventional resources, created by several agencies and companies, with the additional comments and liability of the key-steps in the models. Criteria needed for evaluation of prospective area for shale gas plays, are crucial and thus will be included in the report. A summary for the numbers for recoverable reserves and resource of shale gas in Denmark, Poland and Bulgaria is done in the chapter also. Resource database provided for shale gas potential in Alum Shale as an open-source in the literature by EIA/ARI`s report from 2013[1], urged the need for accurate resource calculations, in which additional factors are covered than the ones given by the agency. The report[1] estimates some 31 trillion cubic feet (TCF) of recoverable shale gas from the Danish Alum Shale, which deemed in contrast of the logical areal extent. On the other hand, the USGS assessment (Gautier et al., 2013)[1] giving the resource potential of recoverable shale gas to be 6.9 TCF, depicted a huge gap between the ARI assessment, and confirmed that less deviation from realistic in-place reserves with newly acquired geological data is a doable task. With new evaluated data, and up-to-date researches, the aim of the paper will be to conclude a most reasonable numbers for Denmark`s shale gas potential, and for the Carboniferous assessment unit in Bulgaria. This will be a strict and very conservative assessment, encompassing all the success risk factors and current socio-economic status of the shale gas/oil exploration industry.

The results from the experiments conducted on shale, siltstone and coal samples from the Carboniferous strata in the Moesian Platform (NE Bulgaria) will be discussed in **Chapter III**, along with the Danish Alum Shale new calculation outcome. Empirical data for investigating of shale reservoir properties such as mineral constituents, porosity, moisture, gas capacity, pore types, maturity levels and depositional environment have been carried in the result phase of the chapter (III). For each case study (Denmark and Bulgaria), different approaches are applied. For Denmark, information from several sources in the literature has been assembled to form a full range of parameters and screening criteria for the Danish part of Alum Shale. This will be the basis for reevaluation of the resource and reserves (GIIP and TRR) for Alum.

Chapter IV is viewed as an explanatory frame for the multidisciplinary approach of economists, policy makers and sociologists. The chapter tends to clarify the potential hazardous implications from using the technology of hydraulic fracturing, current development, and human health while producing shale gas, full-scale of horizontal drilling in the United States, and typical cases with current trends of production. An own overview deemed to represent the future trends in shale gas and oil industry in the U.S. will be presented, along with the socio-economic and environmental concerns for producing shale gas. The prerequisite for this summarized study, will be the latest published reports of David Hughes (2012) in his book “Drill Baby Drill” and Richard Heinberg (2013) with his “Snake Oil: How Fracking`s False Promise of Plenty Imperils Our Future”. The statement of Heinberg (2013) represents the rapid spread of hydraulic fracturing, which according to him “*has temporarily boosted the US natural gas and oil production and sparked a massive environmental backlash in communities across the country*” (Heinberg, 2013)[1]. While, in addition, D.Hughes exposes drilling well data through his report[1], with abundance of figures, explaining the sharp declining rates in the shale gas and oil plays in North America.

LITERATURE REVIEW

In case to provide the full grasp of the main published work in the literature concerning the shale gas development, exploration, comprehensive geological evaluation techniques, experimental analysis techniques and resource assessment techniques, a brief literature review is showed. Because the youthful state of extracting hydrocarbons from shale reservoirs, a critical discussion showing insight and awareness of the different arguments and theories from different publishers, agencies and authors should be gained.

The different approached in the methodological assessment of shale gas resources and reserves, critiques towards the aspects of the methodologies, highlighting of exemplary studies (AOE 2013)[1], emphasize the gaps in the researches, and show how this study will relate to the previous ones, are among the major tasks for the review. The notion for quantitive and qualitative research of shale reservoir properties, parameter and engineering calculations is too wide to be tersely to be bounded in one assessment approach. Therefore, several procedures will be viewed concisely and briefly in the literature screening.

The new exploration targets of unconventional hydrocarbon resources indicate an increase in total petroleum production, after the year 2000. Experts became aware of continuous accumulations first in the San Juan Basin of the U.S., which contained tight-sandstone gas. According to Silver (1950), there was no edge or bottom water in the reservoir structure and the gas is distributed in the Cretaceous formation (Zhang et al., 1999). The discovery of the deposits in western Alberta Basin of Canada, further introduced the deep-basin gas deposit theory proposed by Masters (1979). Rose et al. (1984) argues for the creation of "basin-centered gas" in the gas of Raton Basin, later explored. Experts from USGS for the first time proposed the "continuous petroleum accumulations" in 1995, referring to large spatial dimensions and resources with indistinct boundaries. Schmoker (1996) first provided the gas accumulation mechanism for continuous type of resources, which was the future basis for creating the FORSPAN and volumetric models. In 2006, the United State Geological Survey included deep gas, shale gas, CBM, tight-sandstone gas and natural gas hydrates, as stratification of continuous resources. In addition the U.S. Energy Information Administration changed some of the standards in the methodologies for the first emerging shale gas basins after 1990-th Barnet Shale exploration.

With the evolving technological breakthrough – drilling progress and completion techniques (hydraulic fracturing), construction of pipelines, and shale gas production realized in Appalachian Basin the industry had to adapt new methods for evaluation of resources, and revise the pore-throat storage system of low-permeable organic-rich shales (*Hill, 2000*). The main purpose for the review of the gas storage systems, in this report, is to show the importance of such quality, for changing the values calculated for free and adsorbed gas in the shale reservoirs. *Ambrose et al. (2010)* argued that the type, size and arrangement of the pore-throat system in shale reservoirs alter the storage and calculation of hydrocarbons in place. Similarly *Dewhurst et al. (2002*); *Schieber, (2010); Nelson, (2009) and Zou et al. (2011)*, confirmed that sealing capacity is also affected by pore space, geochemical properties of the shale and amount of free and adsorbed gas in the formation. In addition McCreesh et al. (1991) and Passey et al. (2010) concluded that pore systems in shale have different effects on porosity, permeability and wettability. Thus, it is important for new assessment techniques, to have a study for the pore-throat system of unconventional reservoirs. Also however, *Nelson (2009) and Zou et al. (2010, 2011 and 2012)*, have studied the pore-throat size of different shale reservoirs with nitrogen gas absorption analysis indicating that, the major pore system encompasses pores with diameter of less than 1000 nm. Classifications and categories of pores sizes have been introduced by *Desbois et al. (2009), Curtis et al. (2010) and Loucks et al. (2010).* Conversely, *Slatt and O`Neal (2011)* argue about the former groups of pore types in the shale, by introducing a different approach in the Barnett shale, which imposes organic-porosity and pores between flocculated particles, instead of the given from previous mentioned authors inter- and intraparticle pore types. Further in the report some of those sources will be stated and used for the pore-type grouping.

The presence of large bulk volume of area in shales and gas capacity space, led to new methodological assessment approaches in the shale gas and oil industry. Advance Resource International (2005, 2007) proposed a different assessment type for free, adsorbed gas and oil in collaboration with EIA Outlook annual reports (2007, 2009, 2011 and 2013), with the introducing of success factors for the area assessed, risk oil/gas in place, geological risk, and definition of criteria's for successful shale development such as TOC, net shale thickness, %Ro, brittleness, and others (EIA, AEI2013). The gas-in-place (GIP) and oil-in-place (OIP) methodology provided a more strict and realistic quantification of the shale resources. Nevertheless, the USGS had an old approach proposed by Grace (1995) and Schmoker (1995) called the Analogy method and the FORSPAN, which they started to improve and apply to cases during 2002 and 2005. Klet (2003) improved the methods by changing the database and parameter distribution. On the other hand, Olea et al. (2010) proposed a stochastic simulation method, where he argued that the improvements in the Estimated Ultimate Recovery (EUR) linked to Assessment Units, did not apply in the previous assessments. These three methodologies seem to show some dissimilarity in their predictions, due to different assessment units` type, area delineation, reservoir parameters, petroleum engineering formulas and geological information.

In Europe the funded by companies and associated with the German national geological lab, the six-year shale gas project (GASH) has been started to provide estimation and basin optimization for shale gas resources in Europe. Organic-rich shales have been found in five basins with gas resources of 300 TCF by primary estimation (ARI, 2010). According to Kuuskraa et al. (2009), more than 35 companies are searching for shale gas in Europe – some of which are Exxon Mobil, Devon Energy, Total, ConocoPhillips, and Shell.

Recent researches for the shale gas potential in Denmark were done by the USGS (Gautier et al.2013), with estimated recoverable gas resources in the onshore assessed area of the country 2.5 TCF and 4.4 TCF of gas offshore. The resource is assumed to be contained only in the Alum Shale, deposited in the Cambro-Ordovician period. GEUS along with the University of Copenhagen contributed with the geological input data and models for the USGS methodology and North America resource analogues (*Gautier et al. 2013*). Other studies conducted for the shale potential of the Alum Shale in Denmark were the GASH project (Amin Ghanizadeh et al. 2013), with the experimental study of fluid transport processes in the matrix system of Alum Shale; *Gasparik et al. (2013)* with the investigation of geological controls on the methane storage capacity in organic-rich shales; *Schultz et al (2013)*, with "Biogenic gas in the Cambrian-Ordovician Alum Shale (Denmark and Sweden)"; *Pool et al. (2012*) with his assessment of "*Unusual European Shale gas play: The Cambro-Ordovician Alum Shale", Southern Sweden*; *Nielsen & Schovsbo, (2011)*; *Schovsbo et al. 2013*; and *Petersen et al. (2013).* All those studies in the recent years, contributed to significant determination and allocation of shale properties of Alum and its assessment area delineation. Conversely, to the results of the potential of the Alum Shale and its geological properties, *ARI and the U.S. EIA*, have released their assessment of the technically recoverable shale gas and oil resources in 41 countries outside the U.S. (*EIA/ARI*, *AOE 2013*), different evaluation steps for the resource methodology, and argued that the technically recoverable gas in place from the Alum Shale (Denmark) is *32 TCF.*

As for the total European resources, *Medlock, Jaffe & Hartley (2011),* claim that a TRR in Europe of around 200 TCF is distributed between Sweden, Poland, Austria, and Germany. All of the mentioned sources, nevertheless of the different methodologies of assessment, have dissimilarities in the final results for shale gas and oil potential in Western and Eastern European countries. However, except of the low numbers given by *JRC (2012)* with 250 TCF for a total European shale gas potential, Medlock (2012) with 409 TCF, the high values of *Kuuskraa (2009)* with 1098 TCF and the WEC (2012) with 1118 TCF, there is a hovering pattern around 560 TCF of 8 the other estimates mentioned. In addition, McGlade (2012) realized another trend in 9 other assessment patterns from the European studies of shale gas resources, where the divergence of the results was large. The conclusion of the studies that gravitated around the value of 560TCF is that the utilization of TRR was the value of choice for the majority of authors, which deliberately made it the right comparative value. McGlade (2012) values are scattered between 107-706 TCF.

Nicoletopoulos (2012) and the Bulgarian Ministry for Economy and Energy, estimated 10.5 TCF for shale gas reserves in Bulgaria. For Romania, Hungary and Bulgaria the EIA estimated TRR for shale gas 19 TCF (*Kuuskraa et al., 2011*). On the other hand, Chevron argued that the company can extract up to 8 TCF of shale gas in Bulgaria *(Kuuskraa et al., 2011).*

For Poland the main authors or agencies involved in the assessment with their numbers are as follows: *Donald Gautier et al. (2012) for USGS* estimated the TRR in the Polish-Ukrainian Foredeep of 1.3 TCF (*Gautier et al., 2012*); Kuuskraa (2009) for EIA pointed out that "*Poland has 792 TCF of risked shale gas-in place*"; DERA estimated Poland to contain 187TCF of shale gas resources (*DERA, 2011*); BGR argues that TRR resources in the country are little over 180 TCF (*BGR, 2012*); and Jaffe & Hartley (2011) and Medlock (2012) reduced the value to *104 TCF*.

The master thesis report, will try to clarify the uncertainties in all those assessment types, concluding a mean evaluation method for the shale gas resources in Denmark, by combining several reservoir parameters, and using some of the methodologies, e.g. ARI (EIA) and FORSPAN (USGS). To do so, an investigation of the pore-throat system, and critical parameters of shale`s porosity, free and adsorbed gas, adsorption isotherm, and fluid flows in micro-, macro and nano pores will be conducted. For the Bulgarian case, geological data from the Carboniferous will help in the preparation of the main criteria needed for evaluating the prospective area in the country.

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Special thanks go to Christian Tegner (Aarhus University) for his support in the laboratory, and contribution to the petrophysical properties of shale rocks and clarifying their problematic nature. He introduced me to the experimental and theoretical aspects of natural fractures identification, organic matter in shales and nano-pore systems. Furthermore, he provided the petrographic thin-section visualization and pictures incorporated in the report. I would like to mention Thomas Sørensen (AAU) for giving me the insight for the SEM analysis and inter and intra-particles interpretation and Erik Søgaard for his dedication and organization of the analysis. Ionela Grigoras (AAU) is acknowledged for the preparation and execution of the measurement of the moisture content in the shale samples, and the help provided from her for the interpretation of the results afterwards. I am most thankful to Dorte Spangsmark for her indispensable support with the GC experiment, and the derived data acquisition. Also I would like to express my gratitude towards Kasia Arturi and Rudi P. Nielsen, for their affections towards the problems I have faced with malfunctioning or unavailable apparatus. Special thanks to Heidi Jensen, for solving every administrative issue and for her optimistic mood and consistent help. I thank to the surrounding fellow students and colleagues in Aalborg University Esbjerg, who made the daily routine work easy to handle - Nana, Andreas, Roland, Petya, and Ognyan

Finally, I would like to dedicate this thesis to my family for their permanent support throughout those years.

ACRONYMS, ABBREVIATIONS and NOMENCLATURE

Terms and Abbreviations	Coefficients, Units, Conversion Factors
1P - Proved Reserves	**ΔH – enthalpy**
2P - Proved + Probable Reserves	**Δp – Reservoir and bubble point pressure difference**
3P - Proved + Probable + Possible Reserves	**A – Area**
ARI – Advanced Resources International	**B_g – Deviation volume factor**
Bbbl - Billion Barrels	**C – Constant associated with Poisson`s ratio (equal to 1.91)**
BGR – German Federal Institute for Geosciences	**c3, c7 c – Dimensionless constant (0.0027 and 0.005)**
BGS - British Geological Survey	**cP – Gas viscosity in centipoises**
BP – British Petroleum	**-D – Diffusion coefficient**
Btu – British Thermal Unit	**E – Youndg`s modulus of elasticity [(lbs/in^2)]/(in/in)**
CAPP - Canadian Association of Petroleum Producers	**E – Young Modulus**
CBM – Coal Bed Methane	**F – Force (lbs-force)**
CH_4 - Methane	**F – Fractional constant**
CO_2 - Carbon Dioxide	**g – Gas slippage factor**
DEA – Danish Energy Agency	**G – Shear modulus**
DECC – UK Department of Energy and Climate	**G_C – Gas content (scf/ton)**
DOE - U.S. Department of Energy	**GR_{clay} – Max gamma ray intensity in zone of 100% shale**
EESI - Environmental and Energy Study Institute	**GR_{cs} - Gamma ray recorded intensity at the zone of interest**
EGAF - European Gas Advocacy Forum	**h_{ng} – Height of hydrocarbon column**
EIA - U.S. Energy Information Agency	**k – Permeability**
EROEI - Energy Return on Energy Invested	**k_∞ - Corrected Klinkenberg permeability**
EROI - Energy Return on Investment	**K_b – Boltzman constant (1.3805*10^{-23})**
ERR - Economically Recoverable Resource	**K_b – Bulk modulus**
EU - European Union	**k_{gas} – Gas matrix permeability**
EUP - Estimated Ultimate Production	**L – Length**
EUR - Estimated Ultimate Recovery	**nD – Nano Darcy**
FID – Flame Ionization Detector	**p – Partial pressure**
FVF – formation volume factor (z)	**P_L , p_L – Langmuir Pressure in adsorption isotherm**
GASH – Gas Shales in Europe Project (Germany)	**P_{lt} – Corrected Langmuir Pressure**
GC-MS – Gas Chromatograph Mass Spectrometry	**Psi – Pressure: pounds-mass per square inch**
GEUS – Geological Survey of Denmark and Greenland	**Q – Volumetric gas flow rate**
GIP – Gas in Place Resources	**R - % of total untested area**
H_2S - Hydrogen Sulfide	**r - Mean radius**
HC – Hydrocarbons	**R – Radius**
HI, OI – Hydrogen and Oxygen indices	**r_e – External or drainage radius**
IEA - International Energy Agency	**R_{sh} – Overall resistivity of shale**
IP - Initial Production	**S – Untested area, with chance of adding reserves**
JRC - Joint Research Centre	**S_1, S2, Tmax - Pyrolysis peak indicators (RockEval)**
LNG – Liquid Natural Gas	**S_w, S_o, S_g – Water, Oil and gas Filled Porosity**
MMbbl – million barrels	**T – Temperature in ^{o}C**
N - Nitrogen	**U – Total assessment unit area**
NGL – Natural Gas Liquids	**V_{ad}^{min}, V_{free} – Minimum Adsorbed Gas Quantity and Free Gas**
NOGA – National Oil and Gas Authority	**V_b – Bulk Reservoir Volume**
NORM - Naturally Occurring Radioactive Material	**V_b – Bulk volume**
OGIP - Original Gas in Place	**V_L,n_L – Langmuir Volume in adsorption isotherm**
OM – Organic Matter	**V_{lt} – Corrected Langmuir Volume**
P10, P50, P90 –10%, 50% and 90% success probability range	**VR_o – Vitrinite reflectance, %**
PC – Polarized Content (RockEval)	**Z – Compressibility (deviation) factor**
pH - Power of Hydrogen	**λ – Mean free gas path**
QFM – Quartz, feldspars, micas	**ρ – Density, in cm^3/g**
SEM – Scanning Electron Microscope	**ρ_w – Formation water density**
SPE – Society of Petroleum Engineers	**υ – Poisson`s ratio**
Tcf - Trillion Cubic Feet	**ϕ – Porosity or pore throat diameter**
Tcm - trillion cubic meters	**ϕ_{ker} - Kerogen volume correction (vol/vol)**
TEM – Transmission Electron Microscope	
TOC – Total Organic content	
TPS – Total Petroleum System	
TRR - Technically Recoverable Reserves	
U.S. - United States	
URR - Ultimately Recoverable Reserves	
USGS - United States Geological Shale	
WEC - World Energy Council	
XRD – X-Ray Diffraction	

Table of Contents

1. Introduction to Continuous Petroleum Resources

1.1. Continuous hydrocarbon resources

Over recent decades the increasing global demand for energy has directed attention towards alternative sources for energy, including both “renewable” and unconventional petroleum resources. Unconventional petroleum accumulations are continuous or pervasively charged oil and gas reservoirs that cannot be extracted economically except through implementation of specialized technologies (*Cainengzou et.al 2013*).Such petroleum accumulations include shale gas, coalbed methane (CBM), tight gas, basin-center gas, oil and gas in fractured shale and chalk, gas hydrates, heavy oil, tar sands (oil sands) and shallow biogenic gas (*USGS 2005*).

Fundamental differences exist between conventional and unconventional accumulations:

- Conventional accumulations are found in structurally or stratigraphic defined traps of porous reservoir rocks, sealed by faults and or impermeable caprocks;
- Conventional accumulations are buoyancy-driven, completely separated from the source rock;
- The reservoir in conventional accumulations is in coexistence with the source which encompasses only one formation;
- The continuous accumulations consist of large volumes of rock formations laterally charged with hydrocarbons, and they do not depend on gravitational and buoyancy of water oil and gas for production;
- Conventional accumulations are usually discrete fields, whereas continuous accumulations have large spatial extension and diffuse boundaries (Figure 1).

Continuous petroleum accumulations thus do not form fields in a traditional sense, but *core areas* known as “sweet spots” with enhanced production characteristics within the continuous accumulation.

Geological features of continuous accumulations include their occurrence down dip from water-saturated rocks, large areal extent, variable pressures, absence of trap or seal, and close or direct association with the source rock. The production characteristics include absence of dry holes, poor recovery, immense in-place gas and oil volumes, dependence of fracture permeability, and presence of high productive areas (sweet spots) within the accumulation. Such accumulation show almost static water in the matrix of the rock, but can produce water from fractures.

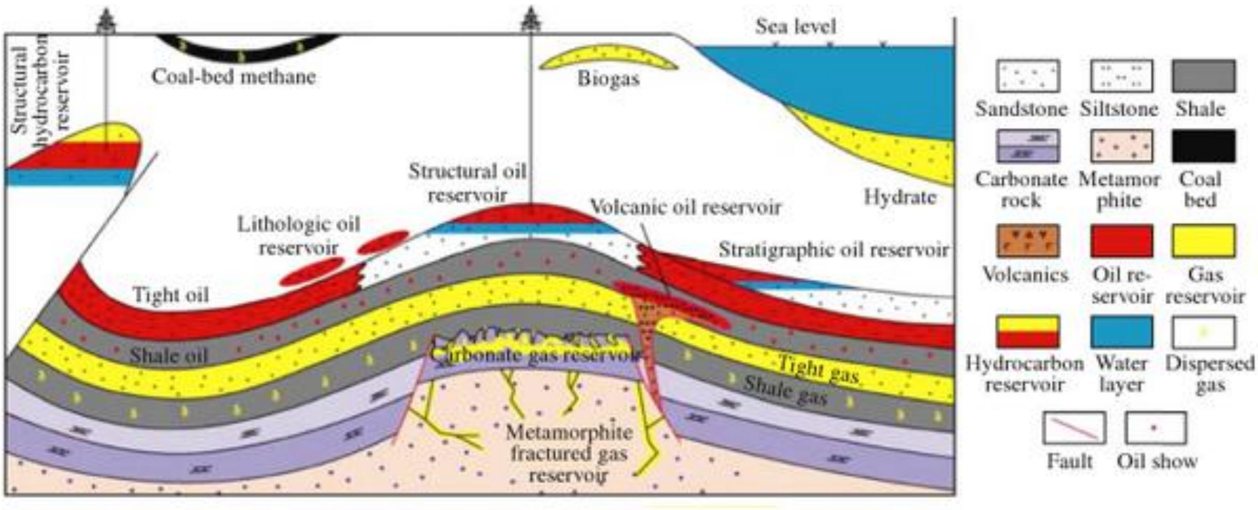


Figure 1 Distribution model of different unconventional and conventional hydrocarbon accumulations (Cainengzou et al.2013)

Unconventional petroleum accumulations are found in passive continental margin basins, foreland thrust zone, and in basins of the foreslope areas of foreland basins. They tend to occur in giant structures in regional slope and basin centers - depressions where vast deposits of petroleum source rocks occur (*Cainengzou et.al 2013*). Assessments of unconventional resources include evaluation of the volume of oil or gas-in-place, finding profitable areas in the basin (sweet spots), specifying their areal extent, cumulative productivity and lifespan of the accumulation. Successful production of unconventional resources (shale gas, tight oil, etc.), requires special technologies such as horizontal drilling parallel hydraulic fracturing (including multizone fracturing of horizontal wells), drilling of multiple wells from a single surface structure. Further key technologies include 3D and 4D seismic surveys, micro-seismic detection and non-Darcy flow regimes in low permeable shales.

1.2. Types of Continuous petroleum resources

Continuous petroleum resources represent large volumetric quantitive accumulations with low total percentage of the hydrocarbons` amount. Others of the same group, poses higher qualitative properties of the contained hydrocarbons, such as heavy oil, oil sandstone, oil shale, CBM and tight-sandstone gas and oil, and thus will be the key future field of development in the oil and gas industry. However, they require sophisticated technology in the phase of extraction. From the continuous petroleum accumulations, the enriched methane hydrates have the higher degree of difficult technologies to produce.

Global unconventional natural gas resources include tight gas, coalbed methane, shale gas, and natural gas hydrates. Along with those oil-prone formations also exist. According to recent research the unconventional gas is approximately 8.3 times than that of the global conventional gas, pointing to a promising future (*IEA, 2009; USGS, 2000l EIA, 2004*). Pointed out in the table below are the major differences between unconventional resources.

Table 1 Differences among Unconventional oil and gas accumulations (Cainengzou et al., 2013)

Characteristics	Shale gas	CBM	Shale oil	Tight oil	Tight gas
Location	Close to sedimentation center of the basin	Distribution area of continental higher plants	Deep sag or shale at slope	Basin center or slope	Basin center or slope
Porosity	<4%-6%	Most less than 10%	Most less than 10%	Most less than 12%	Most less than 10%
Permeability (10^{-3} μm^2)	<0.001-2 x 10^3	Most less than 1	Most less than 1	Most less than 1	Most less than 1
Configuration of reservoir-source rock	Source rocks, reservoirs, and seals are in one	Source rock, reservoir, and seals are in one	Source rock, reservoir, and seals are in one	Reservoirs contact source rocks directly or in short distance	Reservoirs contact source rocks directly or adjacent
Trap	No obvious trap definition				
Petroleum migration type	No migration or proximal migration within the source rock	No migration or proximal migration within the source rock	No migration or proximal migration within the source rock	Primary migration or secondary migration with short distance	Primary migration or secondary migration with short distance
Occurrence	Diffused and gas enriched in fractures	Fracture or cleat areas	Fracture area	Dissolution pores and fracture area	Dissolution pores and fracture area
Seepage	Desorption, diffusion	Non-Darcy flow dominates			
Fluid	Dry gas, absorbed gas in kerogen and pores, free gas in fractures	Absorbed gas dominates, minor amount of free gas	Oil at low-medium maturity	Oil at low-medium maturity	Gas saturation varies greatly, most less than 60%
Resource	Resource abundance is low and reserves are calculated based on the well production				
Exploration technology	Low production, low EOR*, long production period, horizontal wells and fracturing are needed	Low production, low EOR, long production period, horizontal wells and fracturing are needed	Low production, horizontal wells and fracturing are needed	Tight reservoir, low production without fracturing, specific technologies are needed	Tight reservoir, low production without fracturing, specific technologies are needed
Typical examples	Alum Shale in the Baltic Basin (DK) Cambro-Ordovician	CBM in Ordos Basin (China)	Late Devonian Bakken shale in North Dakota and Montana (U.S.)	Eagle Ford shale , North America	Rotliegendes tight-sandstone, NW Europe
***EOR – enhanced oil recovery**					

Tight-sandstone gas was the first one from the continuous resources to be developed and extracted. Nowadays, the span of the tight gas resources account for 70 discovered sedimentary basins with primary migration from shale deposits to adjacent continuous sandstone reservoirs (*Cainengzou et al. 2013*). The distribution of such resources is primarily in the United States, Latin America and Asia.

The development of *CBM (Coal Bed Methane)* has prompted an autonomous unconventional gas sector area, which developed from coal-mines gas extraction. Until now around 35 countries have commenced researches on their coal-bearing methane resources (*USGS 2012*). In-situ deposits of dry coal-gas are distributed mainly in former Soviet-Union, Canada, U.S., and Australia.

<u>*Shale gas*</u> generated immense stress on developing new technologies for exploration of continuous petroleum accumulations recently. The only country that engaged a full commercial exploration and production of shale gas in the world is the United States. At the moment, around 20 shale gas basins have been exploited, which accounts for 17% of domestic gas production (*EIA, 2013*). This along with the shale oil will be discussed in depth during the study.

<u>*Natural gas hydrate*</u> is now at first stage of resource assessment and still has not been yet exploited. The tackle is to acquire suitable technologies for its exploration and production. Geologically, the main area of distribution of those resources is the seafloor of continental shelf margin and the permafrost.

<u>*Heavy oil*</u> reserves are mainly distributed in the Orinoco heavy oil belt (62%) in Venezuela (South America) and the Middle East (18%). However, *natural bitumen (oil sandstone)* is more abundant than heavy oil in global sense. In Alberta, Canada the largest number of resource is concentrated in the sandstone formations. According to BP (British Petroleum) the remaining recoverable reserves could reach 81.8 % of the total remaining reserves (*2010*). The natural bitumen extraction until this date has only been developed in Canada.

<u>*Oil shale*</u> has its history in the unconventional resources development. Production started around 1970`s in several countries rich in oil shale deposits – Estonia, China, Australia and Brazil. The peak of production came around the 1980`s with more than 351 MMbbl (*BP 2011*).

There are several specific accumulation patterns for the variety of unconventional resources, ranging from long distance secondary migration to stratigraphic and short or primary migration. The main accumulation paths and principles for different unconventional hydrocarbon accumulations are summarized in the Figure (2) (left) below. In shale formations, the generation of oil and gas is the main process, forming organic pores, with no or small primary migration length, which forms inorganic pore types (Figure 2) (right).

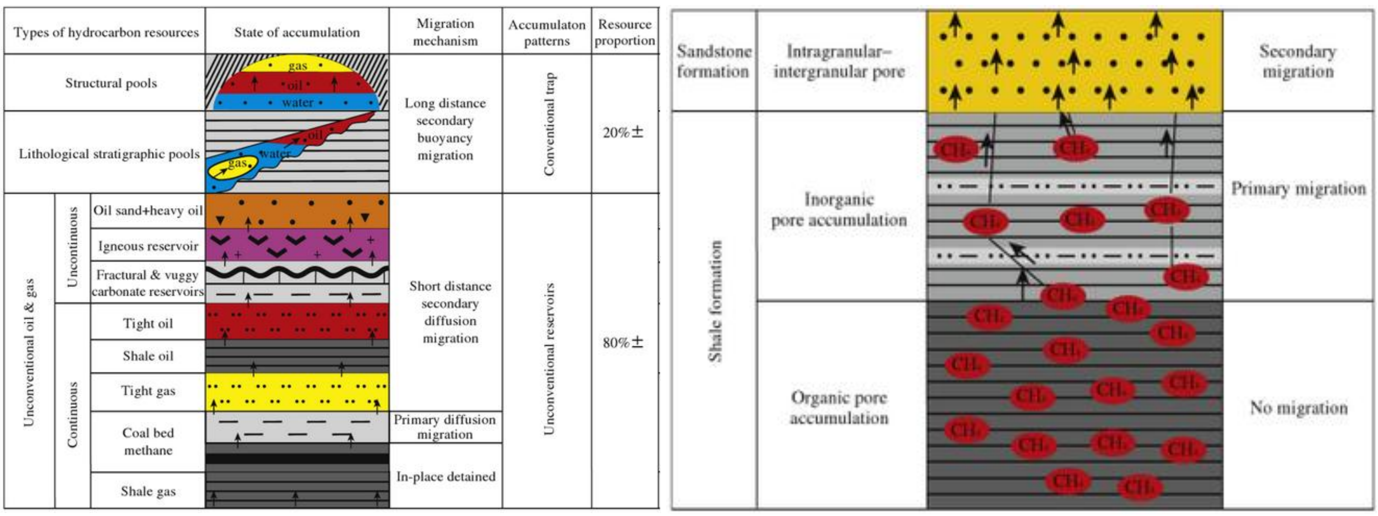


Figure 2 Hydrocarbon resource types and accumulation patterns (left), and shale gas-forming mechanism and model of "saturation reservoiring" (right) (Cainengzou et al., 2013, Book: Unconventional Petroleum Resources).

1.3. Shale as a source rock

Even though the oil and gas industry uses the common term "*shales*", such organic-rich deposits have to be called with their geological proper name – *mudstone/mudrocks*, because no fissile properties exist is the main deep low-permeable formations. Mudstones prevail in the sedimentary record in the subsurface, accounting for about 60-70% of all the Earth`s rocks (*Speight, 2007*).

Shale gas is defined as natural gas from dark organic-rich shale formations that are known to be self-generating and self-preserving in regard to gas. Continuous petroleum shale deposits include also silty mudstone, siltstone, muddy siltstone, and sandstone (as thin interbeded layers in the shale). Different rock types in shale impose different storage mechanisms. The light-gray shales are considered lean in gas, whereas black color is deemed as plentiful in organic matter deposited in oxygen depleted environments with rich hydrogen sulfide portion. The fine-grained fragment (clay and organic matter) in the shale usually has grain diameter of less than 0.0039 mm. The rock is intensively laminated, poorly sorted, finely layered and fissile (the ability to split easily). Laminas can store free gas and provide migration routes for desorbed gas. Several types of pores are developed in gas shale reservoirs, such as: pores in the sedimentary kerogen (OM) pores, intragranular, intergranular and nano-meter pore-throat systems. They can hold large quantities of hydrocarbons when the rank of maturity increases, and the gas phase is released via artificial fracturing of the shale. The three types of gas – free and adsorbed state or in solution (e.g. micropores in bitumen (Bustin, 2006) can vary in lateral distribution. In specific local regions in the sedimentary basin (core areas), the shale formation is usually characterized by distinctive properties, which should encompass important criteria, like high TOC, availability of brittle minerals, large net thickness of organic-rich interval, average degree of thermal maturation and moderate burial depth.

Physical properties in mudrocks are governed by the grain composition, fabric of the authigenic clay (mud), post-depositional processes (suspension, redeposition, bioturbation, and compaction) or diagenesis as whole. The abrupt change in the physical properties of the shale is due to heterogenicy, which changes rapidly the geochemical pattern of the rock in vertical and lateral direction. The laminas in shale are the smallest stratigraphic entities defined which are stacked in beds, bed sets that form parasequences, and finally the combination of which leads to formation development. This layering effect of mudstones causes the anisotropy to vary with its direction of deposition. Anisotropic fabrics in shale deliberately defined by soft components (clay), is intensively found in gas shales due to peak maturity and occurrence of thermogenic gas. The properties of a shale rock (shape, orientation, packing, sorting, composition, etc.) are different in parallel and in perpendicular direction to the layering. This phenomenon can be controlled by seismic data provided by geophysicists to engineers and geologists, and then inputted in various models of potential reservoir mechanisms (fluids, geochemical parameters, etc.).

Higher TOC (Total Organic Carbon) accounts for higher gas content and saturation. A value over 2% for the carbon content (TOC) is usually a lower threshold for prospective shale in the sedimentary basin. Another factor of great importance is the level of maturity, which should be higher than 1.3 $\%R_o$ in order for the shale to have reached the gas generation window. The third main criteria for an economical production of shale gas from mudstone-shale formations is the mineral constituents of the reservoir or the percentage of brittle minerals like quartz, feldspar, calcite, dolomite and plagioclase. More than 30% from the latter should be present in case to achieve successful rock "shattering". The mineralogical groups of pyrite and apatite are considered as neutral for the geo-mechanical behavior of the rock itself. Clays are undesirable bulk material due to their ductility properties. The microstructure of shale is defined by grains with the size of a few micrometers. Clay minerals are among the main constituents in the non-marine shale. When marine shales are first deposited, and then compacted, reduction of pore space commences with aligning the platy minerals in a perpendicular direction to the compressive stress. This results in highly directional mechanical, elastic and transport-bedding properties.

Low organic matter density (depending on maturity of kerogen) can weight between 1.1 and 1.4 g/cm^3 and is usually lighter than bulk shale densities (2.65 g/cm^3). Thus, the organic-rich shales are lighter than shales with low concentrations of kerogen. Moreover, mudstones with interconnected organic matter have lower elastic moduli and higher ductility, whereas isolated-kerogen mudrocks with dispersed kerogen in their matrix system tend to be less ductile (*SPE, 2012*). TOC in shale affects the formation by:

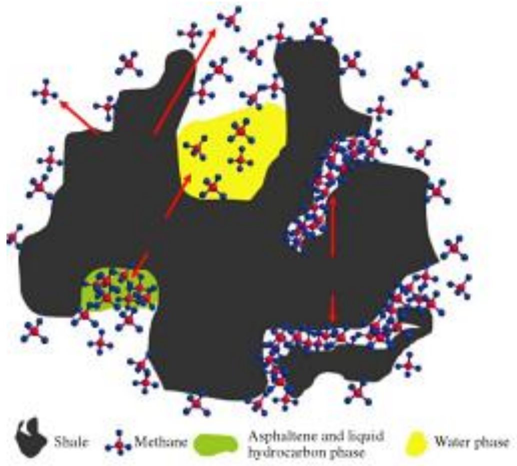
- Lower density and alter wettability;
- Impart anisotropy and introduce adsorption;
- Increase in porosity – shale will have low bulk density when the porosity is high.

Pores in shale are situated in intra- , intergranular and OM void spaces and can contain effectively petroleum fluids. Lamination of the shale formation by high quantity of silicate-clastic (quartz) materials can extend natural or secondary induced fractures. Moreover, some interbeded layers of siltstone and sandstone can optimize the permeability and respectively the reservoir properties. Incrementally filled natural fractures can increase productivity of unconventional gas wells. More than 50% of the total generated hydrocarbons can stay trapped in the shale or mudstone formations. The gas in the shale formation might be situated in the following void structures (Figure (3) - left):

- Local large pores (natural occurring fractures and matrix pores);
- Free gas in micropores (OM and matrix pores) or adsorbed on kerogen and minerals` surfaces (clays);
- Pores as adsorbed gas or dissolution in mould mineral grains;
- Small quantity can be traced in asphaltene, kerogen and saturated gas in the oil.

System Type	Characteristics	Secondary migration	Poro-Perm Components	Examples
1 - Conventional Tight	Tight SS, siltstone, carbonate interbedded w/ lean, immature source rock	Significant	Inter-granular	Spraberry, Lewis Shale, Mancos, Mesa Verde
2 - Hybrid/Interbedded	Tight SS, siltstone, carbonate interbedded w/ rich, mature source rock	Moderate		Bakken, Bone Springs, 2nd White Specs
3 - Porous Shale	Source rocks with significant inter/intra-grain porosity at oil to gas/condensate level of maturity	Minimal	Intra-granular	Eagle Ford, Haynesville, Wolfcamp, Woodford
4 - Fractured Shale	Mature source rocks with significant fracture porosity	Minimal	Fracture	Monterey, Woodford, Mowry, Barnett, Marcellus

Figure 3 Pore system (right), and spectrum in fine-grained reservoirs system (left) (Cainengzou et al. 2013) and (SPE, File 131768, ILC-Tab, 2013)



The diverse occurrence of methane gas in gas-bearing shales (Figure (3) - right) includes different states of presence – dissolved, free and adsorbed. The free gas in shale follows the same pattern as in conventional gas reservoirs, whilst the adsorbed state is more likely to be in the same setup as in coalbed methane reservoirs. Methane adhesion, at temperatures lower than 75^{o}C, is likely to form hydrate structures, while adsorption above 75^{o}C will lead to filling of void pore spaces and water molecules (*Caineng Zou et al. 2013*) (Figure (4) right).

Natural gas in shales is usually dry, sour, and contains natural gas liquids (NGLs – heavier hydrocarbons than methane) associated with gas production, that can vary in gas shales and thus contribute to more profitable extraction. It can conclude non-organic gases such as CO_2, H_2S or CO, which are undesirable components, and are further removed during the gas processing stage by downstream amine scrubbing or gas "sweetening".

Productivity from shale reservoirs can be established after successful completion of hydraulic fracturing in the formation and treatment with multistage repetitive over-pressuring. This will lead to enhanced production rates of the well, due to increased permeability values in the shale. A main factor for defining the properties in mudstone and shale deposits is the geologic control that includes several conditions as schematically represented below (Figure 4).

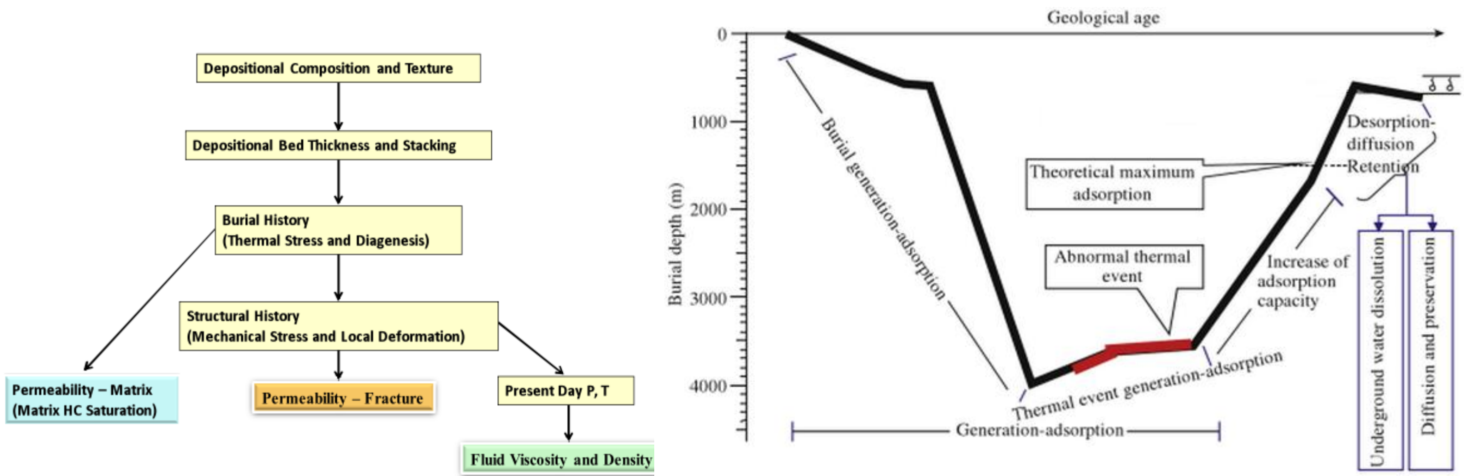


Figure 4 Geologic control on shale properties (left) and evolution and primary mechanisms for shale reservoir formation (right) (Pitcher et al, 2012, SPE 153681, PDF; and Cainengzou et al., 2013)

The paleo geologic setup of a shale formation marks whether a gas or oil-bearing source rock will retain its hydrocarbons, or lose some during the evolution of the basin, which includes faulting, subsidence, fracturing, etc.

Commercial development of shale formation for gas production refers to effective deposit in which there is a minimum amount of 2% TOC, 40% brittle minerals, at least 20 m of net-pay thickness zone and maturity in the gas-generation window (at least 1.3%R_o). In the United States, a minimum net thickness of gas-generation shale is established to be 6 m (Fayetteville Shale), and the maximum is 304 m (Marcellus Shale) (*Cainengzou et.al. 2013*). If the maturity is more than 2.5% (main deliverability for shale gas), that indicates a thermal degradation of the gas and crude oil thermal cracking. Dry gas can be obtained in the early stages of diagenesis when some organic matter is transformed in a biogenic manner, by biochemical aggressiveness of organisms. Otherwise, the remaining OM turns into kerogen with as the burial proceeds and increasing of P/T conditions takes place. In the epidiagenesis, kerogen is turned into wet gas and liquid hydrocarbons, whereas in the meta-diagenesis range a thermogenic dry gas is formed (Figure 4). The in-situ accumulation of gas is then established, where the volatile matter is trapped in the pore system of the shale. That is why referring to shale gas sometimes might be as an in-situ retention reservoir formation (*SPE 2012*).

The recovery ratio in shale gas reservoirs usually varies between 12 to 35% according to the *Editorial Board of Series of Shale Gas Geology and Exploration 2009*. The recovery depends on the formation pressure and the adsorbed gas content. The low migration distances of the hydrocarbons in the shale reservoir, confine the potential drilling areas into small delineation spots with thin bedding. The change from vertical to horizontal direction in the penetration angle during production of shale gas by laterals has been the critical breakthrough for dealing with accessing thin layers. A simple comparison is the initial production of a vertical well - 2800-8000 m^3, to a horizontal one of more than 15000-33000 m^3, speaks for their volumes (*Cainengzou et.al. 2013*). The lifetime of a typical field for shale gas production can reach *30-50 years*. The latest data from *USGS* impose that Barnett Shale in the Fort Worth Basin can have a production cycle of 80 to 100 years (*USGS, 2012*).

The economic viability of shale deposits are expressed by two quality parameters – reservoir and completion (*RQ* and *CQ*). The RQ is mostly dependent on porosity, mineralogy, saturation of gas/oil, formation volume factor (FVF), TOC and thermal maturity, while CQ is governed by geo-mechanical properties of shale, such as elastic stress, Young`s modulus, Poisson`s ratio, bulk modulus, rock ductility, natural fracture distribution, intrinsic and fractured material anisotropy and prevailing magnitudes of stresses. The Completion quality (CQ) is an attribute that can predict the successful hydro-fracturing stimulation during production of shale reservoirs. That is why, in prior of any shale gas production effort and well positioning determination, the most favorable RQ and CQ values (sweet spots) should coincide with the prognoses of the well drilling path. This can be further enhanced by seismic data in the start of the exploration stage.

CHAPTER I – Theory – Shale gas Reservoir Engineering and PVT data

1.4. Shale Gas Reservoir Characteristics

Oil and gas reside in deep rock formations, where permeability is defined as the ease or difficulty of fluids` movement in the matrix, and porosity is the bulk pore volume in which organic matter and fluids are found. Usually porosity and permeability show proportionality in their values. If a rock has high porosity, it also has high permeability and high capacity for oil and gas storage. However in shale, both parameters are usually reversely proportional, i.e. if porosity is high there might not be sufficient interconnectivity in the matrix (low-permeability) and gas or oil resources are not recoverable. This is due to small pore sizes of the channels in the matrix permeability.

In their basic understanding, sedimentary rocks compose of materials derived from erosion of other rocks, which are then transported to a low-lying spot (lakes, embayment, ocean shelves, and subsidence) and accumulated. Layers in the sediments vary in respect to the settling type of particles and geological conditions. Sediments are heterogenic, and thus one lithology changes to another along the bedding plane (gradation or coarsening). The main sediments can be divided to detrial and chemical types (*Donaldson, 2014*). Shale comprises mainly of clay, but the quantity of other clastic sediments and OM can reach 50% from the total bulk shale volume. Clays are detrital type of minerals, formed by erosion processes, degradation and mechanical disintegration of other rocks, which infers of shales being from both of the mentioned types. The alternating shale layers or beds vary in size (from few *mm* to tens of *m*), while the clay particle diameter is 1/256 mm (*Tiab, 2012*). Due to oxidation of minerals, absorption of water, solution in water or the reaction with carbonic acid, hydrous aluminum silicates are formed (*Begum, 2008*). Clays drive from the mechanical change (breakdown) or chemical alteration of three types of *feldspars*: (i) *plagioclase* ($CaAl_2Si_2O_8$); (ii) *ablite* ($NaAlSi_3O_8$); and (iii) *orthoclase* ($KAlSi_3O_8$). The main chemical reaction in vadose areas (soil) and groundwater environments is the natural (e.g. carbonic) acids combined with *feldspars*:

$$2\ NaAlSi_3O_8 + H_2CO_3 + H_2O \rightarrow Na_2CO_3 + 4SiO_2 + Al_2SiO_5\ (OH_4) \qquad (1)$$

Clay sized particles, during the sedimentary transport, are easily washed and suspended in the center of basins or water bodies. Mixing them with organic matter, depositing them in anaerobic conditions with certain degree of burial constitute for the creation of petroleum fluids. Nearly all shales are related to former aquatic depositions and show marine origin.

Shale successions are easily identified among other geological formations, by the use of well-logging methods like spontaneous potential (SP) and gamma logs. The main equation in gas-shales extraction and production with horizontal wells is the one including the well radius (modified Darcy eq.) (*Tiab and Donaldson, 2012*):

$$Q = \frac{7.03.k.h}{\mu_g.z.T} \cdot \frac{\left(p_e^2 - p_w^2\right)}{ln\left(\frac{r_e}{r_w}\right)} \qquad (2)$$

Where q is the gas flow rate $(scf/D)*10^9$, k is permeability (mD), h is thickness of reservoir (ft), p_e is pressure at the boundary of the drainage area (psi), p_w is the wellbore pressure (psi), μ_g is gas viscosity (cP), z is the gas deviation factor, T is temperature in ^oF, r_e is external or drainage radius, *and* r_w is the wellbore radius

The gas found in such formations needs to be released, so that it can flow to low pressure subzones with a production well preceded by special completion stage. Sorbed gas, especially in shale beds, within the OM and reactive minerals is not expelled even when the rock exerts high tectonic stress and pressure gradients. Thus it can be only commercially produced by hydraulic-fracturing completion techniques. Because of the large spatial extent of shales, the geological risk of finding a deposit is low. However the key point is to find sufficiently large occurrences with recoverable quantities. Emphasis on sweet spots in core areas of shale plays, in the Unites States, is now an immense practical application. TOC in those zones is a vital metric of interest in the U.S., where most deposits of shale gas/oil consist of about 4-10 % organic carbon. The high TOC yields more gas quantity in the shale deposits, and it has been found to have close relationship with the porosity and the available gas capacity storage place (S_g) (Gasparik, 2012). Different shale formations experience specific or individual screening criteria between each of the parameters (TOC, porosity, permeability, moisture, etc.). The ratio between the solute, desorbed and free gas is important for evaluating the reserves of gas shales, due to their control on production rates.

Initial shale brittleness contributes to further artificial fracturing of the rock and modification of initially low matrix and pore permeability. This property (brittleness) is driven by non-organic mineral composition. Core sampling of the formation with the establishment of its mechanical properties along with the TOC, thermally maturity level and adsorption capacity, determines its future prospects. Further geological factors tend to regulate the successful shale exploration and production, namely - depth, thickness, pressure (overpressure), gas partial pressure, and favorable conditions for gas retention in shale reservoirs. Common reservoir attributes used for force ranking gas-shale portfolios goes on with the parameters and the desired values for each one of them specified by different screening criteria, which is listed in the table below (Table 2).

Table 2 Common reservoir attributes used for force ranking gas-shale portfolios (after SPE, File 131768, ILC-Tab, 2013)

Parameter	Desired value and result
1. Dehydration Effect (S_w)	< 40 %
2. Depth	Dry gas window in combination with shallow depth
3. Fracture Fabric and Type	Vertical versus horizontal orientation, filled with silica
4. Gas Composition	Low CO_2, N, and H_2S
5. Gas-Filled Porosity (Bulk Volume Gas)	>2% Gas Filled Porosity
6. Gas type (biogenic, thermogenic, or mixed)	Thermogenic (with an oil precursor)
7. Mineral constituents restrictions	< 30% clays , and Biogenic vs. detrital silica
8. GIIP (free and sorbed)	>100 BCF/section
9. Permeability	>100 nanoDarcy
10. Poisson`s Ratio (static)	< 0.25
11. Pressure	>0.5 psi/ft
12. Reservoir temperature	> 230 ^{O}F
13. Stress	< 2000 psia Net Lateral Stress
14. Wettability	Oil prone wetting of kerogen
15. Young`s Modulus	>3.0 MMPSIA

The mineral constituents, not only have to include brittle material (Qz, F) and less clay minerals, but it is preferable that the shale contains more quartz than calcite in its pores and matrix. In addition the "Series of Shale Gas Geology and Exploration and Development" (2009) propose that the minimum shale gas content for commercial development should be 2.8 m^3/ t or 98 scf/ ton.

The thesis will try to investigate and address some basic researches needed on reservoir scale, so that those *"difficult"* rock types (shales) are better understood:

- Source and reservoir parameters of OM
- Physical properties of organic-rich shales
- Sedimentological, diagenetic and structural control of sweet spots
- Multi-phase and single gas flow in different pore and matrix spaces
- Lithological, geochemical and maturity controls on porosity, pore sizes and gas capacity
- Reliability of research methods for studying the shale reservoir properties and assessing the in-place HC

One of the challenging tasks in the methodology and evaluation of the economic potential of a shale gas reservoir is the estimation of the amount of contained gas (GIP), and knowing what controls the in-place resource. The free associated with the porosity gas along with the sorbed one are controlled from the OM quantity, mineral constituents, and are function of the chemical and pore structure of the rock matrix in the reservoir (Gasparik et al., 2013). Other governing factors for the GIP might be the adsorption capacity, transport properties, geochemistry of the rock and moisture content. The gas storage in fine-grained black shales is a complicated multi-parameter system, thus a reliable research and experiments should be conducted carefully.

2. Research Nomenclature of Shale Gas

Most of those critical parameters needed for investigation of shale generative properties discussed previously, can vary with depth, due to alternation of lithotypes in shale, such as TOC vertical change (<1-3 meters), or controlled by stratigraphic changes and biotic factors (*Q.R. Passey, 2010*).Adequate drilling, logging and laboratory experiments need to be executed before extracting and assessing shale gas resources. Analysis techniques for shale reservoirs encompass: XRD, TOC measurement, adsorbed/canister gas analysis, vitrinite reflectance, core and thin-section descriptions, porosity, permeability, fluid saturation, and scanning electron microscopy (SEM) analysis. Once laboratory results are obtained, logging responses are added on well-log suites (density log, resistivity log, and gamma-ray log), so the full parameter range of shale is described. Screening criteria that filter the empirical data and which are of most importance for successful development of shale gas and oil are expressed in the table below (Table 3). Their identification through laboratory experiments and engineering calculations is crucial for the production of shale gas.

Table 3 Description of needed investigations of reservoir parameters for successful shale gas development and measurements done in this project

Shale Reservoir Parameter	Characteristics	Effect and importance on shale gas development	Investigation method or measurement type	Equivalent research executed in the study for BG
1.Free and adsorbed gas capacity	Sorption capacity, moisture content, porosity, permeability, pore system types and gaseous state	Available void space for gas storage in shales, adhesive properties of gas, moisture effect on gas capacity, diffusion and desorption mechanisms, defining the flow regimes in fractures and nano-pores and crucial criteria for amount of gas that can saturate the shale	Langmuir adsorption Excess isotherm, He manometric expansion SEM Core Data Analysis for measurement of ϕ and k	Scanning Electron Microscopy (SEM) Moisture Content
2. Geo-mechanical properties, fracturing capacity	Poisson`s ratio, Young modulus, effective stress, ductility, brittleness, mineral constituents, Qz and clay content, anisotropy, heterogency of shale, matrix and cement type and rock mechanics	Defining the potential of shattering of the shale in the completion stage, compaction stress-strain identification, bulk mineral content, elastic and shear stress percentage, vulnerability to fracturing, and clay dehydration level during diagenesis	XRD Core Mechanical Tests Petrographic microscope analysis of thin- section SEM	Petrographic analysis of thin-section SEM
3. OM abundance and maturity rank	TOC %, OM origin, kerogen type, %Ro, gas precursor and type, quantity of OM, marine or non-marine shales, and biomarkers identification.	Identification of % of organic matter, biogenic or thermogenic gas, depositional environment, type of kerogen (I, II, III), H index, CO_2 and CH_4 quantity, vitrinite reflection for gas generation window and gas chromatogram for quantitively defining the gases present.	GC-MS, RockEval analysis, Vitrinite Reflectance (%) Elementary Analysis	Gas Chromatograph RockEval analysis
4. Depth and Prospective Area Distribution maps	T and P gradients, net thickness, areal extent of the resource, cross-section maps, seismic profiles	Defining the net thickness interval of organic rich shale, overall seismo-stratigraphic profile, burial depth, formation pressure of reservoir, capillary pressure, clay richness, hydrocarbon interval identification	Gamma well logging Resistivity logs, Neutron logging Seismic survey, Stratigraphic cross-sections and Litho-stratigraphic analysis	Gamma Log (indirectly) Stratigraphic cross-sections (indirectly)
5.Geological conditions for gas retention	Reconstruction of paleo-geological sequences, burial history, structural and tectonic regime, erosion, uplift, subsidence, reservoir depressurization	Paleo-geological maps and main events in the geological past exerted on the specific formation, burial depth for reaching the temperature range to cook the kerogen, risk of gas retention due to depressurization of reservoir at shallow depths	Paleo-geological reconstruction maps Litho-stratigraphic analysis Depth profile and burial history	Litho-stratigraphic analysis, Paleo-geological maps of the Moesian Platform

2.1. Geochemical and geological generation, transformation and deposition of OM

Organic residue left from plants and animals, which is composed from C, H, O and N, is broken down by bacteria. The deposits precipitated in aquatic environments with low oxygen index (lagoons, lakes, seas or deltas), are protected from aerobic bacteria, and therefore exposed to anaerobic micro organisms. The material then is mixed with different lithotypes – sand, silt, clay; accumulate, compressed and transformed. This is the primer stage of the transforming of the organic matter, which yields *kerogen*. Due to intensive subsidence during former geological periods, the sediments are exerted to high pressure-temperature conditions and buried below thick rock mass. Kerogen transforms into hydrocarbons by thermal breakdown (cracking), causing oxygen and nitrogen to be expelled and only the HC structure to remain. From temperatures approximately around 50-60^{o}C, kerogen is turned into petroleum (oil), until 120-150^{o}C, from which point the oil is subjected to further thermal degradation and transformed to wet- and then dry gas (Figure 5). Light hydrocarbons are an indication of either a high temperature burial history or longer exposure to thermal cracking, because only the shorter molecules remain in the chain, and then form the light components (like paraffins).

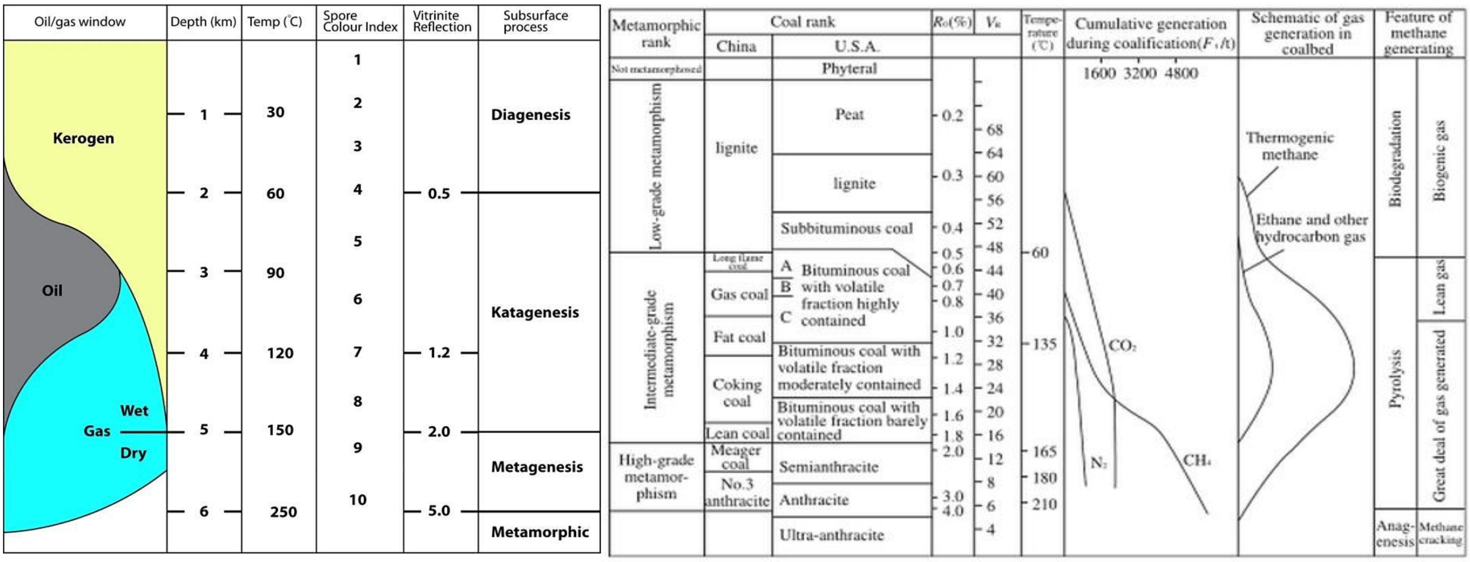


Figure 5 Evolution of organic matter: Diagenetic, catagenetic and metagenetic processes, along with comparison of the processes with relative intensities of light reflected from the coal maceral vitrinite (left) and division of coalification stages(right) (Cainengzou et al., 2013; and Almandi, 2013, Shale gas in Europe)

The high pressure exerted by the source rock is the controlling factor for generation of hydrocarbons, and the kerogen expelling mechanism referred as primary migration. The likelihood for retention of oil and gas phase in the fine-grained sedimentary rock is the basic reason for exploration and production of gas from organic-rich shale formations.

Petroleum is formed mainly in catagenesis (Figure 5), where the transformation depends on the organic matter type and time-temperature history. Thermogenic hydrocarbon gas is generated at greater depths than 2 km, and is the desirable gas (with an oil precursor) for the continuous gas shale reservoirs. Coal is also dependent on time and temperature for its maturation. The measure of the change of the vitrinite (maceral), by the intensity of reflected light at nominal wavelength of 546 nm, is the reason of using the maceral as a thermal history marker. Vitrinite reflection is then correlated to the maturation of oil (Figure 6). The vast occurrence of vitrinite makes it a main biomarker for sediment rocks containing fossil fuels. Total content of OM (organic matter), which includes kerogen and bitumen, is given in terms of the total organic carbon content (TOC) in mass percentage. It represents the whole quantity of carbon atoms and the ratio of their mass to the total rock matrix mass. Thus, for making a conversion into generated and expelled petroleum masses, one should have the mass of the total source rock.

Generation of petroleum is a decomposition reaction, including variable mixtures of kerogen, macromolecules and lighter hydrocarbon molecules (*Hantschel 2009*). The kinetics of petroleum is recognized by cracking types (primary and secondary), kerogen types (I-IV) and the number and type of the hydrocarbon component (bulk, oil-gas, etc.). According to the abundance of some elements, such as C, O, and H, the kerogen is chemically combined into groups. Most common types are H/C and O/C ratios originally used in coal maceral classifications, firstly used by van Krevelen (1961), who gave the resulted three main kerogen types known today – I, II, III (Figure 6).

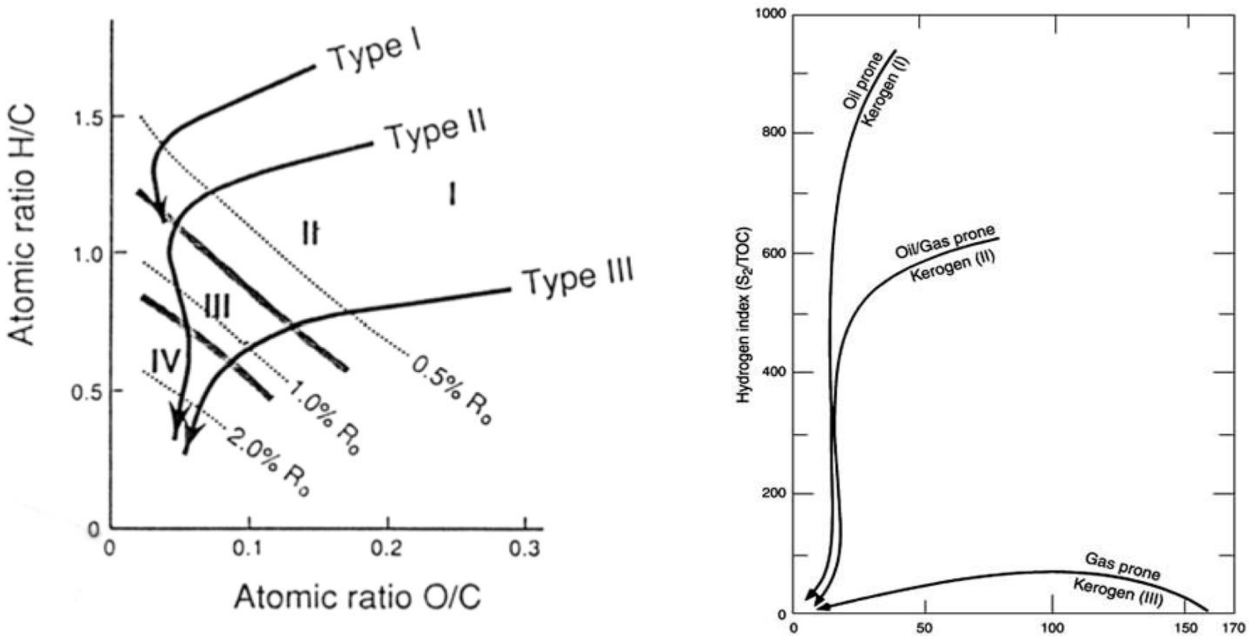


Figure 6 Characterization of kerogen by van-Krevelen diagrams – (left) abundance of the elements in kerogen in ratios of H/C and O/C; (right) generative amounts of HC and CO2 in RockEval parameters HI (hydrogen index) and OI (oxygen index) (Krevelen, 1947)

The kerogen types are also linked to depositional environments and the province of sedimentary influx. Type I is from lacustrine algal matter, but also some petroleum source rocks deposited in marine setup, experience the appearance of this kerogen. Type II is the most ubiquitous one. It is an indicator for marine sediments, with autochthonous organic material (in-situ) in a reducing environment. Type III kerogen has the highest relative oxygen content, indicating terrigenous environments, from plant organic matter. Type IV kerogen has low HI values. Low maturity coals usually contain kerogen type III. The generated HC and CO_2 masses of a kerogen sample are measured by RockEval pyrolysis in terms of HI and OI potential, which sums the van-Krevelen diagram components.

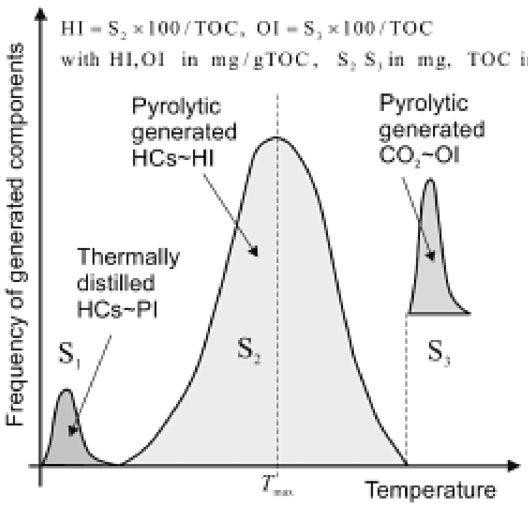
2.1.1. Experiments and interpretation of OM in shales

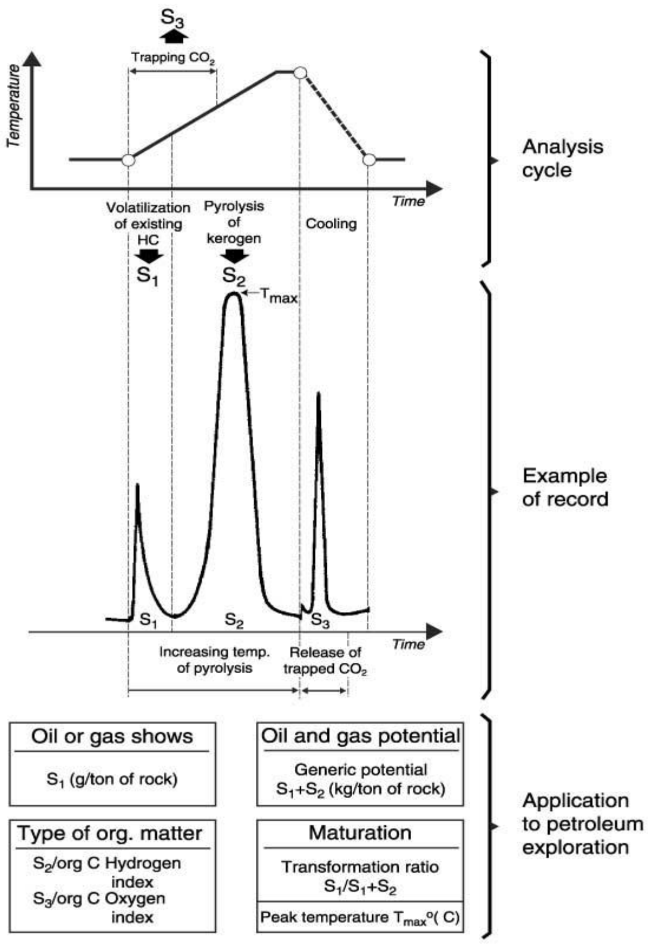
2.1.1.1. RockEval measurement

The RockEval experimental method practically consists of an open system pyrolysis, which is used for identification of the type and maturity of organic matter and detects petroleum potential in sediments. Samples with the accompanied organic matter are heated at around 50 K (25°C/min) per minute, and then a measurement of the released masses of hydrocarbons and CO_2 conducted (Figure 7). After the isothermally kept oven at 300°C, the free hydrocarbons are volatilized. The peak named with S_1 is the first occurrence of thermally distillated hydrocarbons and corresponds to the residual bitumen or the already generated and not yet expelled mass of hydrocarbons (*Hantschel 2009*). The temperature is then increased from 300°C to 550°C, where the second peak (S_2) illustrates the pyrolitic generated hydrocarbon amounts and represents the total generative mass and potential of hydrocarbons, which is related to the hydrogen index (HI), given in mg/g TOC. If the HI is multiplied with the TOC and the rock mass, it will yield the total generative mass of the hydrocarbons in the rock. Rich hydrogen organic matters are dominated by oil generation, whereas poorer of hydrogen OM is mainly gas generative. The third peak (S_3) is the pyrolitic generated carbon dioxide, which is related to the oxygen index (OI) measured in mg/g TOC. The production index (PI) equals to S_1/ [S_1+S_2], where it represents the measure of cracked kerogen, expressed between the values from 0 to 1, and is used for characterizing the evolution level of the organic matter. Pyrolyzable carbon (PC = 0.083 x [S_1 + S_2]) corresponds to carbon content of HC volatilized and pyrolyzed during the analysis. Another special value obtained from the RockEval method is the oven temperature T_{max} at the maximum hydrocarbon generation rate for S_2 (Figure 7). The value of the temperature can be applied for the maturity parameter of the kerogen sample. Maturation of OM can be estimated by the location of HI and OI on the graph below and by the T_{max} range (T_{max}= 400°-430°C represents immature OM; T_{max} = 435°C-450°C represents mature oil zone; and T_{max} > 450°C represents the overmature zone).

It is not enough only to classify the kerogen to the van Krevelen types and guess the composition of the generated hydrocarbons. Further factors should be considered to precisely determine the petroleum yielded, such as anoxic or oxic environment, marine or deltaic facies, biological activity, and others. That is why Jones (1987) introduced the term *organic facies.*

Figure 7 Schematic program from the RockEval pyrolysis. Hydrogen Index HI, Oxygen Index OI, and Production Index PI. Peaks S1 and S2 contain hydrocarbons mainly, and are measured by flame ionization detector (FID). (Nelson D.R. 2010)





This review of the RockEval method is introduced because of the need to familiarize the reader with the experimental and empirical background of the research for such samples. Further results from shale/mudstone samples will be discussed in the case study section for Bulgaria, where the outcomes of such experimental data will be represented.

2.1.1.2. Vitrinite Reflectance (VRo)

Vitrinite reflectance provides an assessment of thermal maturity in rocks younger than Devonian Age. VRo measurements are necessary compliment to TOC analyses. In rocks that are older than Devonian, reflectance of graptolites, chitinozoans, scolecodonts, and bitumen can be measured and subsequently converted to a vitrinite Ro equivalent (in %) for comparative purposes. That is also the case for the values shown in the literature for the Alum shale succession data for VRo, which will be discussed in the case study section.

Maturity is the index for identifying if the organic matter is oil or gas-prone and the degree of its transformation from OM to petroleum products. Ro>1.0% represents oil generation peak, and Ro>1.3% is the gas generation stage. The Ro values for U.S. shales vary between 0.4% and 4.0%, which is evidence for full-cycle of the converting process of OM to hydrocarbons. Higher maturity leads to higher gas-deliverability and higher quantity of gas, while low maturity levels express low gas content. By defining the Ro value, the type of gas can be also determine, when linking the genesis to certain organic matter (biodegradation, thermal cracking, thermogenic and mixed gas). In shale reservoirs the dominant gas is from thermogenic and thermal cracking of crude oil. This is a result of the higher depth; therefore high temperature exerted on the rock and qualitatively cooked organic matter. The favorable prospects for shale gas should be located inside the thermal gas-generation window, where Ro is between 1.1% and 3.5% (Jarvie et al., 2007).

2.1.1.3. Gas chromatography

Gas composition is determined by gas chromatography (GC). Samples are injected into a heated zone, vaporized and transported as a volatile phase from a carrier gas (helium) into a packed column or internally coated with static liquid or solid phase, resulting in separating the injected sample constituents. After elution, the compounds are carried to a detector, which responses on the component concentration to the area of the curve under the detector. Quantitively peaks can be identified by evaluating their retention time inside the column with those of already identified compounds previously analyzed at the same GC calibration specifications. Thermal conductivity detectors (TCD) are commonly used in the apparatus, because they can also detect non-hydrocarbon components in gaseous mixtures, such as nitrogen and carbon dioxide. The flame ionization detector (FID) thus is used more rarely and only for gaseous mixtures without any inorganic gases. The packed columns used have great efficiency range, determining concentration as discrete compounds by hundreds of equilibrium stages.

Such experiment was conducted for the samples collected from North Moesian Platform (Bulgaria), to identify any occurrence of dry gases and some non-hydrocarbon compounds.

2.2. Geo-mechanical properties and fracturing capacity of shale reservoirs

Geologic controls play substantial role in defining the properties of mudstone and shale reservoirs. Because of the continuous lateral extension of such formations, the depositional composition and texture are highly determined by bed thickness, stacking, thermal stress and diagenesis. Along with those processes the structural history of the region in the geologic past is important too. Mechanical stress, local deformation and subsidence along with fault-fracture systems control the matrix permeability, pressure and temperature exerted by the reservoir, viscosity and density of the hydrocarbon fluids in the shale and mudstone deposits. The source rock and the reservoir can be characterized and positioned in vicinity of each other, either adjacent or interbeded. Organic-rich rocks having either a gas- or oil-bearing patterns, may be close to the same formation, without its organic-rich facies, or interbeded with non-organic rich beds.

The bulk mineralogy of shales and mudstones, affects the geo-mechanical properties of such formations, and is in great importance for the completion stage of commercial production from shale gas wells, where the hydraulic fracturing takes place. The criteria of the depositional environment of the shale deposit for the evaluation of the dominant mineral types can be narrowed down to whether the rock is a marine or non-marine. Marine deposits usually have lower clay content and high brittle minerals - authigenic quartz, feldspar and carbonates. Thus, those types are favorable for hydraulic stimulation because of their brittle nature, and easy induced artificial fractures. The terrestrial (non-marine) shales, such as fluvial, deltaic, lacustrine, etc., have higher clay content and are stiffer, ductile and require higher pressures for their response to fracturing.

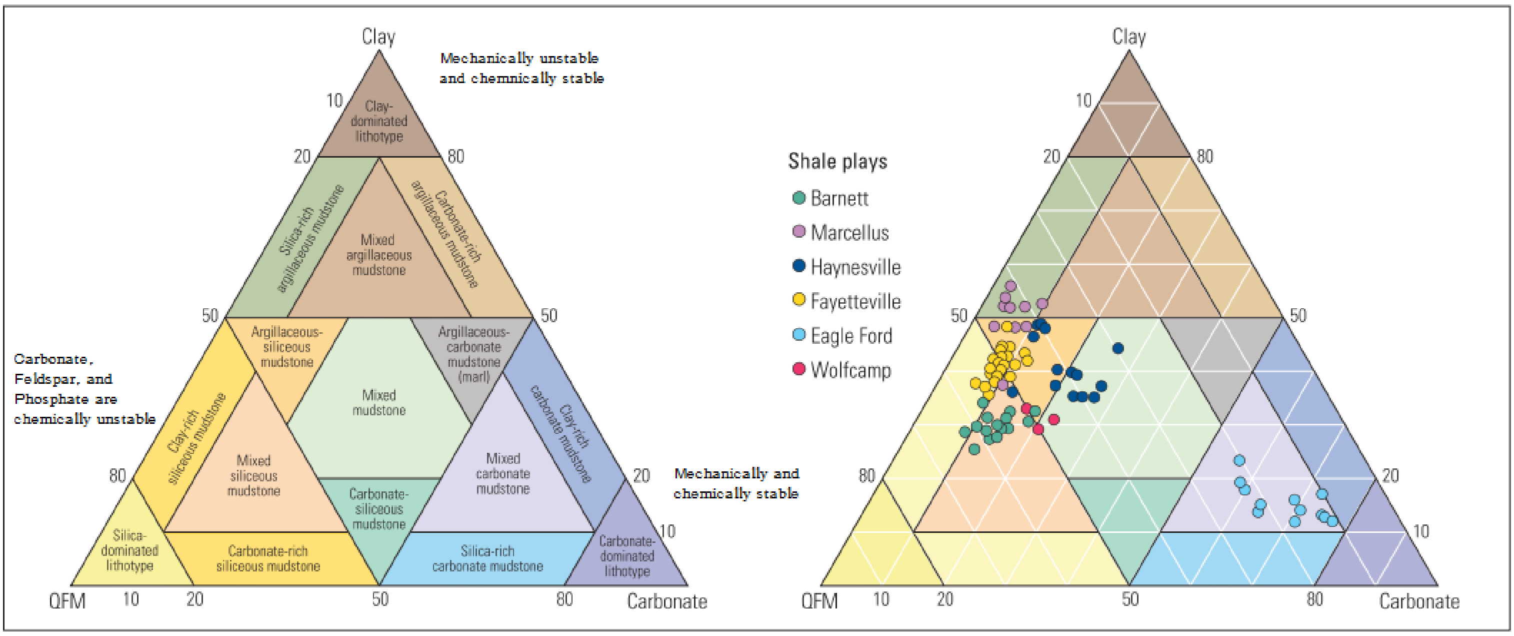


Figure 8 Compositional diagram for mudstones showing relationship between mineral and members (left) and a Ternary diagram of shale mineralogy for specific shale plays in North America (right)(sCore classification tool).The corners of the ternary diagram (left) are clay, carbonate and quartz plus feldspars plus micas (QFM). 16 classes of mudstones based on the mineralogy are defined. Mudstones in the right part of the figure are sought by oil companies, and tend to have less than 50% clay. (Schlumberger sCore , Boyer C, Kieschnick, 2006))

When estimating the prospective area of continuous petroleum deposits (such as organic-rich shales), it is crucial to comply the history of the geological region and the burial depth of the formation. In the prospective area of a shale play assessors include depth of the formation between 1,000 and 5,000 m (*EIA, ARI 2013*). This is because, areas shallower than 1000 meters, tend to have low reservoir pressure and no mobilizing of the hydrocarbon fluids migration (buoyancy, diffusion or segregation). Those shales (<1000m.) have mainly a water saturated fracture systems, which lowers the cross-sectional pore area for hydrocarbons. Whereas deeper than 5,000 m deposits, tend to have the likelihood of reduced permeability in the matrix system with high pore-throat spaces in the nano-meter scale, which leads to high drilling and production costs. The interaction of water with carbonaceous rocks can lead to physisorption onto polar surfaces, and chemical sorption on mineral surfaces. In shale, the water content has influence on the polar clay mineral surfaces. Chalmers and Bustin (2007), suggested that such interaction can be found with a relationship to organic matter microporosity and clay mineral surfaces. Furthermore, the pore volume (micro pores) within shale formations with substantial quantity of clay minerals in their bulk composition, can be increased because of the internal surface area that they provide for additional sorption capacity. In addition, the sorption capacity of clay minerals decreases in the following order: smectite> > mixed layer I/S > chlorite > illite, with larger sorption energy for methane on kerogen than the one exerted in clay minerals (OM>>>smectite).

2.2.1. Rock mechanics of shale formations

Rocks experience both horizontal and vertical stresses in the lithosphere because of overburden and tectonic stresses. Due to pore pressure the pores in shale can contract or expand to a small degree, due to change in capillary and pore pressure, as the poro-elastic theories of *Geerstma (1953*) explain.

Elasticity is known to be the possibility of increasing and decreasing the volume of any fluid or material and is expressed as the ratio of stress (force per unit area in N/m^2) to strain (deviation in the deformation from the initial length and width). The three main types of deformations are the Young`s, Bulk and Shear modulus, where the first one defines the change in length ($\Delta L/L$), the second the change in volume ($\Delta V/V$) and the third the change of angular shape (tan s). The inherent forces in molecules and atoms resist deformation and thus compact under pressure (compressibility), or they extend (until certain level) when subjected to a tensile force. Furthermore, the space between the molecules in a molecular group is different, this is why some fluids are incompressible and others compress. Gases have high compressibility because of high distance of the molecules from one another, whereas solids have decreased compressibility (elasticity however is opposite of compressibility). The elastic waves produced from the oscillation of molecules under tensile stress (strain) will travel with certain velocity. Solid materials experience stagnated molecular reactions, meaning that the molecules won`t change their position but only vibrate in place, and thus generate a longitudinal wave (compression or pressure wave), which has velocity of up to 7.5 km/s in limestone, and transverse waves (shear mode), which moves up and down and has speed of 3.6 km/s in limestone. Only solids can transmit waves composed of shear motion (S-waves), while gases and liquids transmit the compression waves (P-waves). Those elastic properties are the fundamentals for seismic surveying and geophysical evaluation of shale formations.

The orientation of the shale bedding of the deposits, can determine the mechanical properties for each formation. Due to the laminated structure of the rock high tensile stress is exerted. The elastic moduli of a material is primarily described by its Poisson`s ration (υ) and Young modulus (E). When a rigid (solid) body is constrained is a certain space, and a force is applied to it, then the body will exert elastic deformation. The strain is a consequence of three stresses: change of length with respect to the initial size ($\Delta L/L$), the change of diameter (radius) of a cylinder with respect to initial radius of the rock ($\Delta r/r_o$), and change of volume (Islam et al. 2013) (Equation 3).

$$Young`s\ Modulus\ (E) = \frac{Stress(\sigma)}{Strain\ (\varepsilon)} = \frac{F/A}{\Delta r/r_0}\ \left[\frac{N/m^2}{cm/cm}\right] \tag{3}$$

$$Hooke`s\ Law\ \ \frac{F}{A}(\sigma) = (E)\frac{\Delta r}{r_0}(\varepsilon) \tag{4}$$

The representation of Hooke`s Law is integrated because of the need to define the stress of an elastic body as proportional to the strain applied, depicted as the constant of Young`s modulus (E). This means that if an elastic cylinder is not confined, the strain deformations (in lateral direction) will be equal to the stress applied (F/A), and the slope of the line is equal to the Young`s modulus ($E = \Delta\sigma/\Delta\varepsilon$).

Planes of weakness in the different deposits can be critical for natural fractures to occur in folded structures (anticline or syncline). Along those planes, the rock may fracture, because of its geomechanical properties (alignment of phyllosilicate due to overburden diagenesis) and lead to higher potential to fail in the slip surface (*Aadnoy et.al 2009*). Almost every shale formations shows a dynamic anisotropy, thus why the permeability is also expected to be anisotropic in the different dimensions in the strata (mainly parallel to the bedding) (Figure 9). Tensile strength can vary widely, but usually has values in the vicinity of 0.51 to 0.87 MPa (*Islam et al 2013*). On the other hand, according to *Soreide et al. (2009)*, the downhole undrained stiffness for North Sea shale at 140°C is 57% of the stiffness at room temperature. The latter also showed empirically that the stiffness for the shales with loading parallel to the bedding (E_P) is higher than for loading perpendicular to the bedding (E_T). That is the main argument for the abrupt and ubiquitous heterogenicy of shales.

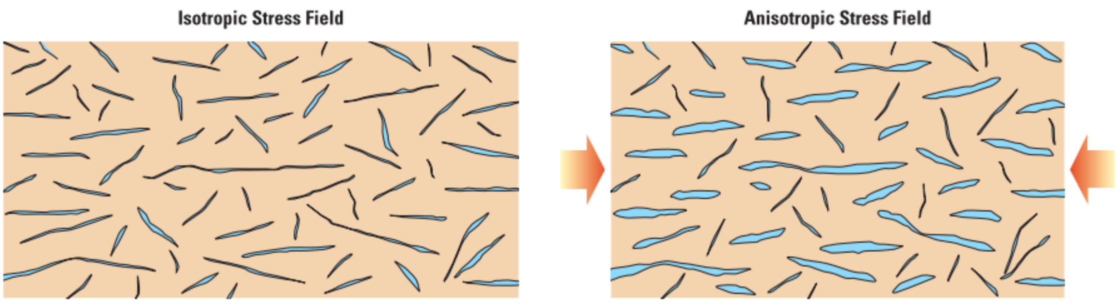


Figure 9 Isotropic and anisotropic stresses in heterogenic shale formations (Donaldson, 2013, PDF, Hydraulic Fracturing)

Because of overburden stress, and the heterogenic materials contained in shales, the compressive force usually closes the natural micro-cracks. That is why for rock formations the Hooke`s law is not really applicable because the stress and strain relationship is not anymore proportional, but if a diagram between the two modes is depicted, it will have an S-shape pattern (Figure 10). In such depiction, three autonomous regions can be identified, before the rock experience shattering at the ultimate point of failure of the formation (the point in which usually hydro-fracturing is processed) (Figure 10). At low stress-strain ratio (Region I) micro-fractures start to close, then the deformation of grains yield an almost linear relationship between the two parameters (Region II), and finally as stress increases new fractures are produced, until the formation reaches its point of failure.

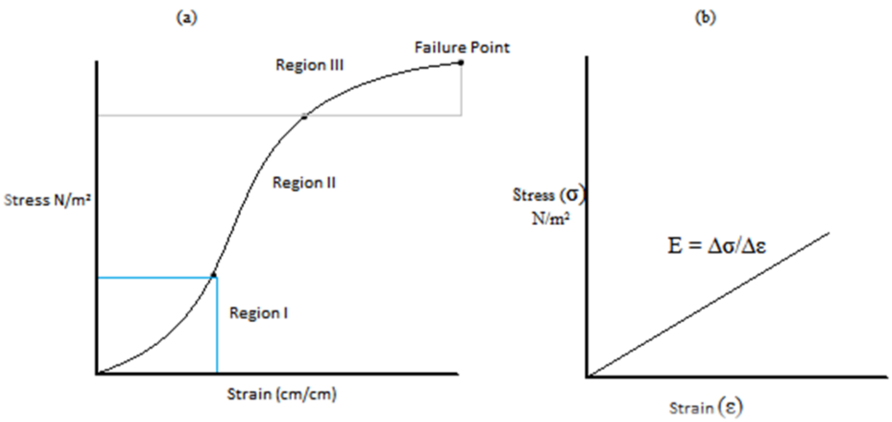


Figure 10 Stress-strain relationship of a rock (a) and Hooke`s Law (b). In the Hooke`s law diagram (b) the stress is proportional to strain and the slope of the line is equal to the Young`s Modulus of elasticity, while in (a) the stress-strain relationship of a rock (a) and Hooke`s Law (rock is different in every region. In Region I, the plastic strain is caused by closure of micro-fractures, in Region II the elastic compression of the rock matrix material, and in Region III the plastic strain caused by micro-fracture formation in response to applied stress until failure (After Hooke 1988)

Poisson`s ratio (υ) is the ratio of the lateral to axial strain (Equation 5). If a cylindrical body experiences an overburden stress (σ_z), it will cause the radial expansion due to lateral stress and lower the size of the body in length along the axial direction (z- axial strain):

$$\upsilon = -\frac{\varepsilon_{lateral}}{\varepsilon_{axial}} = -\frac{\Delta d/d_0}{\Delta L/L_0} \quad \left[\frac{in/in}{in/in}\right] \qquad (5)$$

The main factors controlling the completion stage success are the fractures and planes of weakness that can affect the propagation of artificial fracture stages (hydraulic fracturing). By those parameters, the fracture conductivity may be predicted before any production is executed (Figure 11).

Due to change in the lithology of the shale formation, the gas production rates also vary considerably even when the vertical wells where changed with the hydraulic fractured stages of a lateral well. Nonproductive stages can be up to

50% in total, which is a substantial loss of capital per well. Stress changes as a function of lithotypes, so engineers should prevent the fracture stage to cross a lithology barrier. To do so, they divide the well into segments (clusters) during the fracking stage into similar lithological types. This secures that the specific stage is contained in the specific segment, which confines the length of the fracking-stage to a certain value. Numbers and deliberately monitored parameters are set, so that the main clustering stages are evaluated. Different tracks (Figure 11) are studied, and stress variations are then assigned with a tolerance of 0.01 psi/ft (*USGS, 2013*). This is a crucial step to account for heterogenicity of the shale in the completion design and modeling.

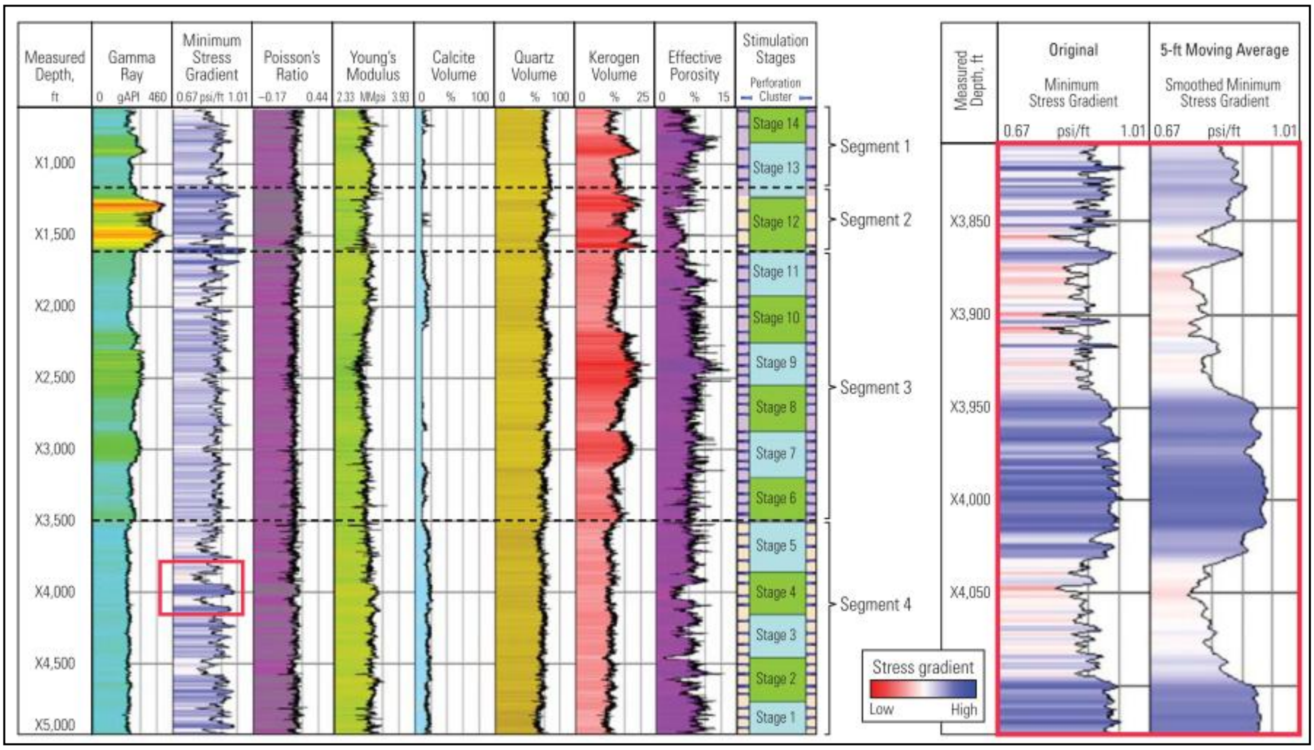


Figure 11 Completion stage simulation with well plan logging tools - segments, stages and clusters of hydraulic-fracturing stage presented by the dependence on the stresses exerted by the shale formation. Track 9 represents the simulation stages with the perforation clusters (short horizontal lines to the stages), where as *Track 2* sets the distance between the clusters with a minimum horizontal stress gradient. In the right side of the figure a close up of *Track 2* shows the high (blue) and low (red) stress gradients. (Line, T. B. (2013). Oil & Gas Spotlight Reserves Matter)

2.2.2. Investigation methods for mechanical properties of shale reservoir

2.2.2.1. X-ray powder diffraction (XRD)

Bulk mineralogic composition is derived from X-ray diffraction (XRD) patterns, which can be measured on a differently-orientated pulverized rock samples. Its main purpose is to determine composition of rocks and other crystalline material, along with evaluating the amounts and types of clay minerals for shale reservoirs. After milling the samples, for the assurance of even grain sizes, ethanol is added to avoid dissolution of water-soluble components and strain damage, along with corundum (20wt %) for precise measurement of the apparatus. The quantities and present minerals are recognized by the diffraction patterns, recognizing the peaks of crystalline structures with interpretation software, and reporting the outcome in weight percentage. This comprehensive quantitive mineralogic study should be executed on shale rock samples, for revealing the clay content in the sample, along with other dominant minerals. Clay-size fraction is analyzed separately from bulk components, and then recombined to provide the total composition of the rock. The crystalline structure can control the sorption capacity, while the minerals involved can affect the brittleness.

2.3. Gas capacity – sorbed and free gas in shales

This section will try to clarify the confounding and complicated nature of adsorbed state gas in the meso-, micro-, and nanopores and further explanation of the effect of Langmuir isotherm, moisture effect on porosity and adhesion of methane, which are primer methods for identification of shale properties and characteristics of variable thermodynamical and kinetic states of gas presence in shale. Quantification of the amount of storage capacity, that includes adsorbed and free gas is a prerequisite for calculating the shale gas resource and technically recoverable reserves (TRR) in a given reservoir. Reliability of sorption data for porosity, organic and inorganic matter`s complex pore structures and pore sizes is now only done by HPHT (High Pressure High Temperature) experiments.

The free, adsorbed, dissolved and liquid-like state gas, are all found in the shale matrix and porous space. The shale gas in the adsorbed state can be found on the surface of pores, as adsorbed molecules, while the dissolved gas state occurs in formation water, as dissolute matter. In shales, during lithification and diagenesis, first the adsorbed gas is formed, then the dissolved one, and finally (after saturation) the free gas is liberated in the pore network. In specific cases, when exact P/T conditions are met in the shale, the three gaseous states tend to be in dynamic equilibrium system (*Cainengzou et al. 2013*). This phenomenon occurs when the petroleum generation increases, or the termobaric conditions fluctuate. The predominant gas state in most shale is the adsorbed one (up to 70%), whiles the free gas accounts for 10 to 20%, and dissolved gas being a rare case (*Song et al., 2005*). Due to high capillary forces in unconventional reservoirs, poor connectivity of crystalline pores and physical sorption on the inner and outer surfaces of OM and minerals in the shale matrix it is likely low flow rates to occur during production of shale gas. Moreover, desorption, dissolution and migration of the adsorbed state into free (porosity) gas can depend on salinity, temperature, pressure and forces between molecules.

Due to attraction forces on the surface of minerals in the shale matrix, adsorption film is created on their top monolayer, which controls the adhesive properties of gas in pores and the matrix (*Collins, 1991*). In the adsorbed state in shales, the gas volume does not have a linear relationship, but it more a function of pressure of the shale gas reservoir (*Cainengzou et al. 2013*). The calculation models are mainly kinetic, thermodynamic and potential theories. Kinetic theories include the Langmuir equation in adsorption to a monolayer of molecules, also known as isothermal adsorption. The following equation (7) can be used for calculating the adsorption properties of shale methane (*Langmuir, 1916*):

$$\mathrm{V_{ad}} = \frac{V_L P}{P + P_L} \qquad (6)$$

$$\mathrm{V_i} \frac{V_{Li}P_i}{P_{Li}\left(1+\sum_j^m=1 \frac{P_j}{PL_j}\right)},\ \mathrm{i} = 1,2,3,\ldots \mathrm{m} \qquad (7)$$

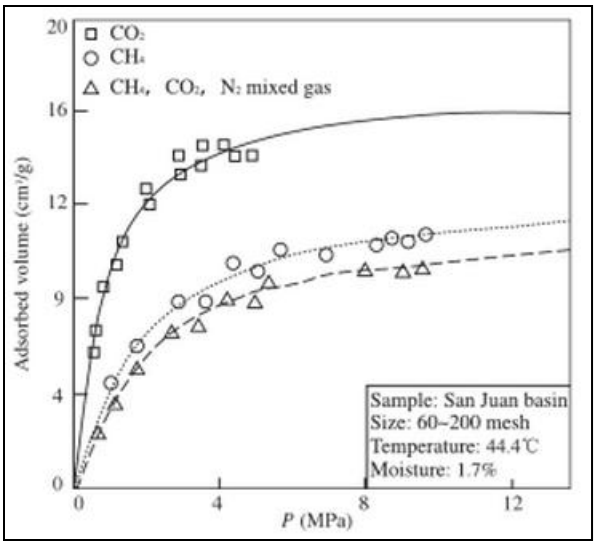


Figure 12 Adsorptive features of has with different compositions (Cainengzou et al., 2013 – Unconventional resources, page 111)

Wherein V_L is the Langmuir volume in m^3/t, reflecting the maximum adsorptive capacity of the shale deposit; P_L stands for the Langmuir pressure in MPa (or psi), at which the adsorbed volume had reached 50% of the maximum adsorptive capacity; and P is the system (formation) pressure of the shale reservoir in MPa (or psi). The second equation (Equation 7) is given because it accounts more precisely for the quantitive relationship in the kinetic adsorption model of Langmuir with adding a multi-component gas system (Figure 12) with mixed and adsorbed state, where V_i is the adsorbed volume of gas composition *i*, m^3/t; V_{Li} is the Langmuir volume of gas composition *i*, m^3/t; P_{Li} is the Langmuir pressure of gas composition *i*, MPa (or psi); P_i is the partial pressure of gas composition *i*, MPa (or psi), related to the mole ratio or volumetric concentration of the mixed gas composition, and *i(j)* and *m* are the mixed gas composition and compositional fraction (*Cainengzou et al. 2013*). In that sense, if shale gas is composed only of methane, *m* will be equal to 1. More realistic and ubiquitous case in shale gas reservoirs is the combination of three types of gases: methane (CH_4), carbon dioxide (CO_2) and nitrogen (N_2), where *m* will be equal to 3, and the equations will need to be modified and calibrated to the current composition state. Langmuir constant can be derived from single-gas experiments at isothermal adsorption of solo gaseous state (*Cainengzou et al. 2013*).

The capacity of adsorbed gas in the shale is not only controlled by depositional nature, maturity level, minerals, stress and pressure gradient, but also by outside-system factors, such as moisture control, temperature and pressure

(*Corsdale et al., 1998*). Mainly two tendencies exist in the shale gas reservoirs in regard to capacity of adsorbed gas (*Gayer and Harris, 1996*):

- When values of Ro% are relatively small, the adsorption capacity increases with rise of the level of maturity
- When Ro% values are greater than 2, the adsorption capacity decreases with rising rank of maturation

The typical linear relationship between Langmuir volume and the volatile component content, infers for increase in the component`s quantity with decrease of Langmuir volume (drop in adsorption volume) (Cainengzou et al. 2013). The higher moisture content diminishes the free spaces (adsorption capacity) for gas in shales, thereby decreasing the gas-capacity (Figure 13). After finite moisture increase, no implications for the system take place, but a plateau stage after the so called critical value (C) occurs, with no adsorption capacity decrease. A relationship between vitrinite quantity (OM) and adsorbed gas can be monitored in some shales and coals (Figure 13), with highest adsorption capacity on the kerogen (OM) in shales and vitrinite in coals.

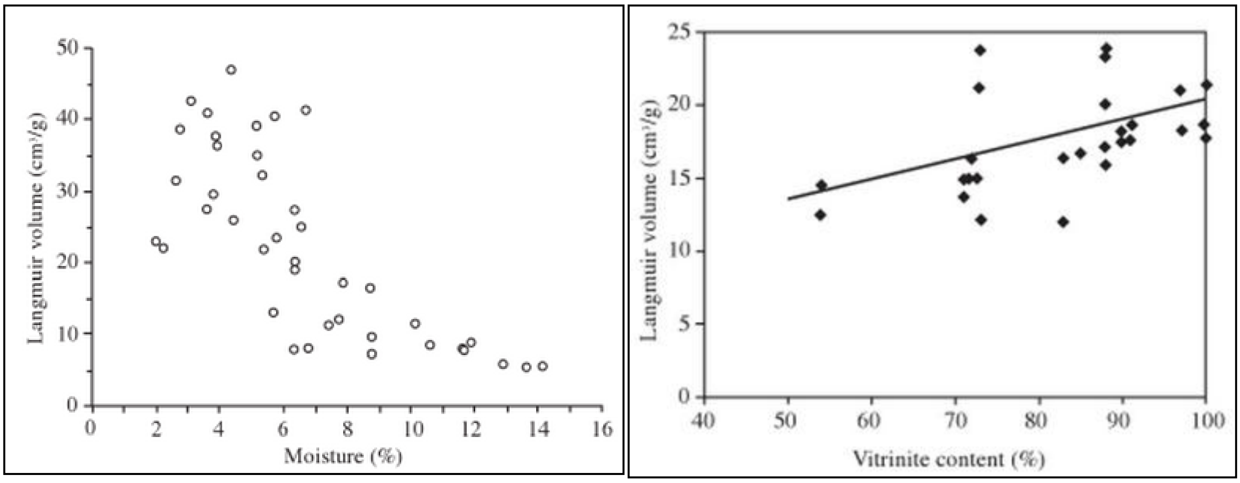


Figure 13 Relationship between Langmuir volume and moisture (left) and Langmuir volume and vitrinite content (right) (Cainengzou et al., 2013, Unconventional Petroleum Geology, Book, Page 112)

The temperature exerted in shale reservoirs does not have a major influence for the adsorption capacity, but can trigger gas desorption (*Cainengzou et al. 2013*). As the temperature increases, so does the free gas. At isothermal conditions, the adsorbed gas capacity of shale (CH_4) increases as the pressure elevates. At a specific pressure range, the adsorption capacity of shale becomes saturated and does not increase further (Gasparik et al., 2012) (Figure14).

The dissolved gas state in shale occurs as gas dissolved in water, with its volume depending on the fluid volume in the rock. Experimental studies have shown that solubility of natural gas compositions are sequential (Cainengzou et al. 2013) – $CO_2 > CH_4 > N_2 > C_2H_6 > C_3H_8 > C_4H_{10} > C_5H_{12}$. Usually the solubility of CO_2 is 36 times that of methane, which has higher affinity to solute than C_2H_6 (ethane). If brine formation waters exist, depending on its salinity and mineralized rate, the solubility can be affected rapidly. If there is an increase in salinity of the water, the solubility of gas drops, where in contrary, if the formation water is from inorganic salt type, it does not influence the natural gas solubility significantly (*Liu, 1998*). The relationship of solubility with pressure is non-linear and positive, while with temperature, solubility experiences reversely proportional type of correlation. Decrease in solubility with rise in temperature is typical for shale reservoirs, but with further temperature increase, at the inflexion point of 80^{o}C the solubility also increases (*Cainengzou et al. 2013*). Some of the dissolved gas in the water, after it had been fully diluted, can be expelled by the external abrupt condition changes into the free gas state in pores and fractures. Even though oil has dissolution capacity to gas, the methane dissolved in oil is usually in negligible amount. Therefore, dissolved gas in shale reservoirs is a function mainly of pore space (volume), methane solubility, and water saturation (S_w).

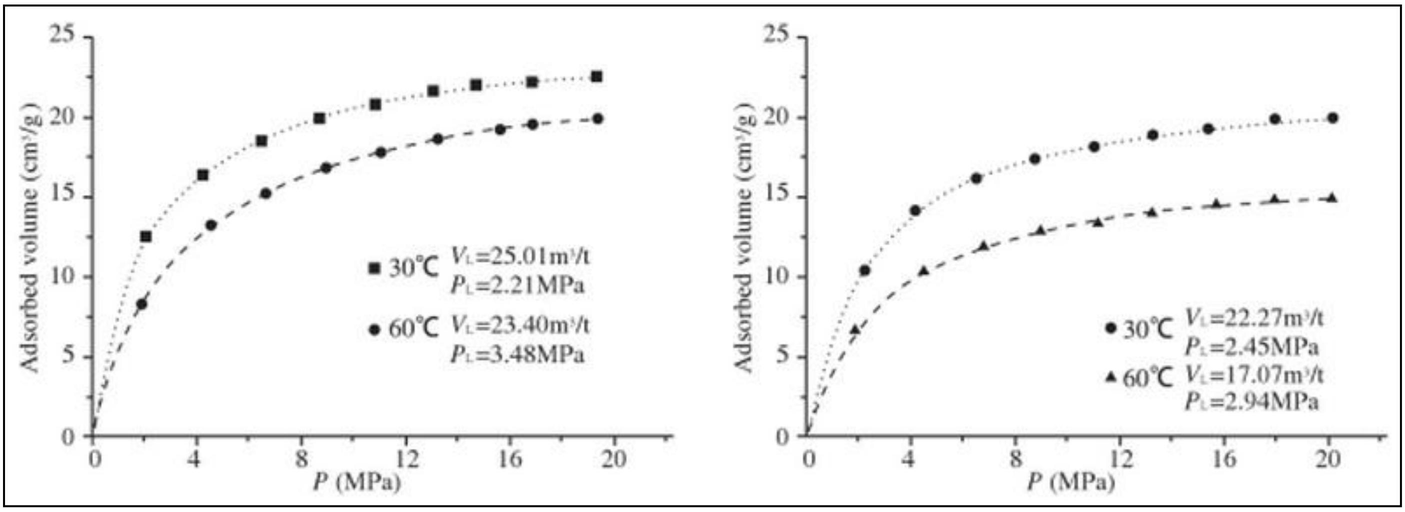


Figure 14 Isothermal adsorption curves at different pressures (Cainengzou et al., 2013, Unconventional Petroleum Geology, Book, P. 98)

Shale gas in free state, situates in fractures, fissures, macro- and mesopores in the reservoir, due to its high mobility, and is calculated by the accumulation potential of free gas as the result of the total accumulation volumes of gas components (*Cainengzou et al 2013*):

$$V_f = \sum_{i=1}^{m} V_{fi} \qquad (8)$$

Where:

- V_f -is the accumulation potential of free gas given in cm^3/g
- V_{fi}- is the accumulation potential of component *I* in free gas, cm^3/g

At standard conditions (ambient termobaric) the gas is assumed ideal, however at reservoir conditions, methane can be regarded as real gas, with slight deviation. If the termobaric conditions are higher, the bigger will be the deviation from ideal gas behavior. Thus, a correction value is represented for calculating the formation volume factors (FVF), expressed as compressibility factor. It should be accounted that the deviation factor (z) of any component of gas, is a value that is correlated with gas, temperature, and mole density.

During the desorption stage of methane, as the pressure is diminished, the adsorbed gas molecules gain energy E_a, to overcome the adhesive potential, and thus are transferred into molecules of free gas. This characterizes the desorption mechanism as an endothermic reaction (*Nodzenski, 1998*). Desorption potential increases as the temperature rise, so does the kinetic energy of the adsorbed gas, and the thermal movement of methane molecules (*Cainengzou et al. 2013*). This phenomenon of Langmuir adsorption isotherm was described and discussed above. If the formation pressure in the shale reservoir is lower than the critical desorption pressure, the gas is in undersaturated case, and its molecules can be desorbed from the inner surface of pores (*Rupple and Grein, 1974*; *Vishnyakov and Piotrovskaya, 1998*). Physical desorption is composed of four subsequent categories (*Cainengzou et al. 2013*):

- *Pressure-reduced desorption* – adsorbed methane molecules of the inner surface of shale matrix pores become active due to decline in pressure, liberating the gas from the attraction forces of van der Waals, causing change from adsorbed to free state;
- *Temperature-elevated desorption* – refers to increase in temperature, that causes higher kinetic energy, acceleration of gas molecules and enabling the methane to be expelled with more power from the binding forces.
- *Displacement desorption* – refers to replacement of adsorbed methane molecules from non-adsorbed water or gas molecules, which set kinetic equilibrium and change the state of gas.
- *Diffusion desorption* – is a diffusion-driven desorption, due to concentration difference

From all those desorption mechanisms the pressure reduced one has major influence in shale gas production, and is important for simulating the flow patterns of gaseous states in the reservoir. Diffusion mechanism is characterized by

Fick`s law, Darcy's law and Klinkenberg phenomenon, all representing the movement of molecules in shale gas reservoirs, due to uneven flow regimes, and different concentration zones.

As gas molecules are enriched on the interfacial layers between gas and solid (adsorption), thanks to the interaction between the two molecules by weak forces (physisorption), energy is emitted during the process that is higher than enthalpy of condensation, which for CH_4 = 8 kJ/mol (*Atkins, 2006*). The common term "sorption" includes the absorption (integrated molecules in a solid structure), adsorption and dissolution processes. The lack of technology that measures the structure and size of sorption state, led to the implementation of Gibbs excess sorption (surface excess) (*Sircar, 1999*).At specific termobaric conditions for a monosystem (comprised only by one gas component), that is in contact with a solid adsorbent (m_s) with certain mass and flat surface, the excess sorption can be defined and characterized in the way of the figure below (Figure 15). The density (ρ) of the volatile molecule on the depiction is larger at the interface area, and tends to decrease once it reduces its proximity to the wall. As the distance (z) grows, the gas phase gradually becomes less dense. However, at certain "z" the effect on the gas molecules derived by the solid surface diminishes strongly and becomes zero. That is the time when the density equalizes with the bulk (free) phase density, ρ_{bulk} (at certain P/T). The combination of the volume for the free phase (V_{bulk}) and adsorbed phase (V_{ads}) represents the void volume ($V^0{}_{void}$) in the figure (Figure 15).

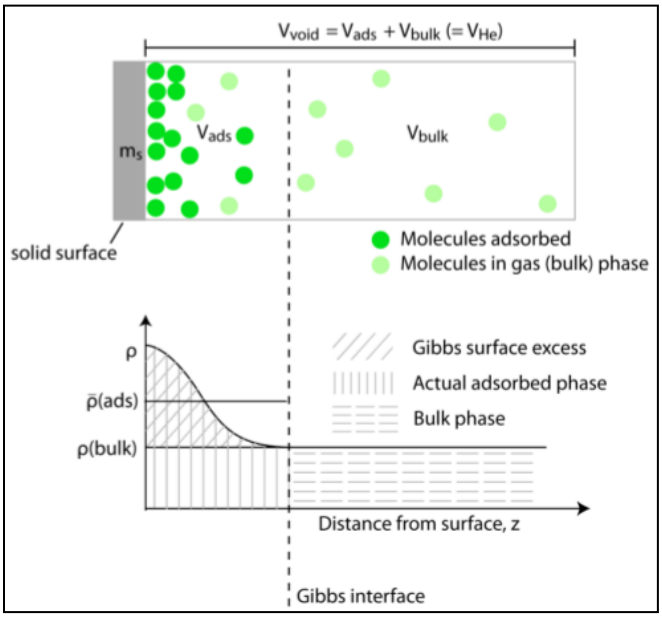


Figure 15 Gibbs concept of excess surface sorption of a flat adsorbent surface. The sketch below in the figure depicts hypothetical density profile that is perpendicular to the adsorbent surface. Bulk density (ρbulk) and density of average adsorbed phase (ρads) are represented to occur on both side of the Gibbs dividing surface. (Keller and Staudt, 2005, Gasparik et al., 2013)

In conclusion, the flow patterns of shale gas production can be summarized as categories of: <u>desorption-diffusion-Darcy flow</u>, which is based on the mechanism of a recovery theory, such as <u>water drainage-depressuring-desorption-gas production,</u> when flow rates are established, thus giving different development stages of the gaseous states in the reservoir (*Cainengzou et al. 2013*). The complexity of real reservoir systems does not allow reproducing full in-situ conditions stages in laboratory experiments. Processes like adsorption, absorption and dissolution are controlled by many geological factors, external attributes (pressure and temperature) and geochemical characteristics of the rock (TOC, mineral constituents, maturity level). Even though, the shale gas reservoirs mainly consist of methane, still some small quantities of other light-hydrocarbons (ethane, propane) or non-hydrocarbons (CO_2 and N) may exist in the pores, which will lower the overall void space (sorption capacity) of CH_4 due to competitive storage (*Gasparik 2013*).

The evaluation of the gas capacity (for both free and adsorbed gas) is the most important task in calculation of the potential of originally gas-in-place (OGIP) shale gas resources, which minimizes the geological risk (success factors) in the exploration stage. Lately, dynamic simulations of the basins have influenced the assessment methods, with which overall forecasting is established, including parameters like pore pressure evolution, structural movements, burial history of the strata, migration and generation of hydrocarbons and others. Thus, the fundamentals of such complex rock environment should not be disregarded.

2.3.1. Investigation methods for sorption capacity and shale pore-throat systemc

The method of adsorption isotherm and the data obtained from it, can result in calculating the "total" storage capacity or the organic component of the matrix, and thus can be a key in unconventional shale gas formations for proper evaluation of their economic value. Furthermore the physical interactions of gas molecules with reactive minerals, viewed under a scanning microscope, can enlighten the manner of desorption mechanisms.

2.3.1.1. Langmuir adsorption isotherm

Adsorbed gas in shale can be present in the organic matter or in primary and secondary porosity systems. The total GIP (free and adsorbed) can be estimated by core samples that are drilled, sealed in canisters and examined in laboratories. First, the gas is removed from the canister, volumetrically measured and compositionally analyzed as a function of time (Ludlow, 1978). For calculation of the in-place resource, the extracted gas over certain time interval is measured in the core sample upon reservoir conditions. The evaluation of adsorbed gas itself needs a volumetric engineering estimation that takes into account pressure relationships, from which the sorption potential of shale can be derived. For the experiments, the samples need to be with increased surface area (done by pulverizing), then heated to eliminate the adsorbed gas and exposed to methane at high pressures and isothermal conditions. The volume of methane adsorbed by the shale, given in scf/ton, results in the Langmuir Isothermal Curve (Figure 16). When the constant temperature plot is obtained, the gas capacity of shale can be calculated by referencing the pore pressure of the formation, which is the actual formation pressure. Engineers use Langmuir isotherms from well cores to compute the adsorbed gas from log-derived TOC data[1]. The free gas volumes are estimated from log-derived effective porosity and S_g after subtracting the computed pore volume occupied by the adsorbed gas[1]. For the evaluation to be precise, other parameters have to be synchronized: geochemical properties, input of clay minerals, matrix density, formation water and bound water resistivity, effective porosity and others.

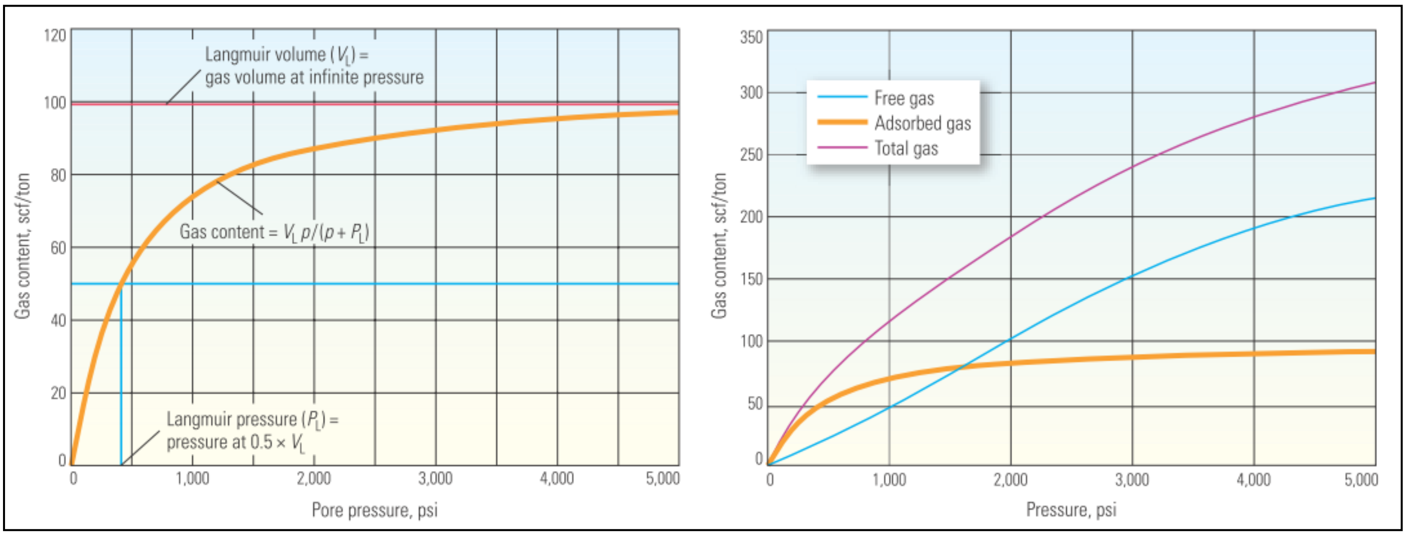


Figure 16 Langmuir isotherms and gas storage capacity. The Langmuir isotherm (gold, left) is derived from crushed rock samples and quantifies a rock`s adsorbed storage capacity. The Langmuir volume (VL) (red line), is the theoretical limit for the gas adsorption at infinite pressure. Storage capacity at given pressure, p, can be determined from the plot. The Langmuir pressure (P_L) (vertical blue line) is the pressure at half the $V_{L.}$ Using the Langmuir isotherm, the GIP (free and adsorbed) for a specific reservoir can be calculated as a function of pressure (magenta, blue). Low pressures provide effective conditions for adsorption gas storage mechanism, while increased ones favor the free (pore) gas. The productivity of shale reservoirs is mainly driven by volume of pore gas. Desorption becomes important when reservoir pressure decreases during production (EIA/ARI, 2013, Outlook Review on Shale Gas, PDF)

2.3.1.2. Excess sorption measurement - Manometric Helium Expansion

Excess sorption is derived from the difference of the whole gas in the system and the amount of gas that would be present if there wasn`t any sorption (bulk gas, with density equivalent to ρbulk at specific P/T conditions that matches in V0void). Experimentally, the excess sorption can be calculated by volumetric (manometric) method with helium expansion prior to the experiment. The gas that is transferred successfully through the volume into the sample cell (cumulative gas) has to be evaluated (Atkins, 2006).

All the experiments conducted on sorption measurement acquire the excess but not the absolute sorption isotherms (*Sircar, 1999*). A quantitive calculation on absolute sorption cannot be made, because of no distinct boundary between the two phases exists (free and adsorbed). Once the excess sorption is derived, a correction of the volume and density of the adsorbed phase has to be implemented, so that the absolute sorption can be at least quantified ambiguously (Gasparik, 2013).

2.3.1.3. Porosity and Permeability experiments

Porosity measurements in shale formations are hard because of the small pore-throat diameters and large surface area (with associated surface water). In addition, mineral constituents in shales like smectite clay contain interlayer water in mudstones, which complicates the evaluation of Sg, Sw and So, but high-level mature shales can diminish the smectite content by ilitization due to exposure to high depths and temperatures. The electron microscopy is needed in order to recognize the nano-pore throat network in shale contained in the OM, which sometimes accounts for 50% of the total void porosity space, with oil-wet pores in some maturation levels.

Permeability is the most difficult parameter for evaluation in shale. It ranges from 0.001 to 0.0000001 mD in mudstones. In shale reservoirs it is controlled from effective porosity, hydrocarbon saturation and mineral composition. Permeability in shale rocks cannot be measured by the conventional percolating fluids through core volumes, but needs to be quantified by ultralow permeability analysis. This includes the use of short duration nitrogen-injection falloff test[1], which accounts for the matrix permeability and the influence of natural fractures. Along with permeability values, numbers for filled porosity, water saturation and grain density can be acquired.

2.4. Depth, Maturity and Distribution polygons for shale reservoirs based on well logs

The vast number of petrophysical properties of shale that are used in evaluation of shale gas potential for economic production, lateral drilling wells, completion stimulation of the well by hydro-fracturing, and others, depend on well-log analysis and core samples of a certain shale bed. Because of complex fracture network, sharp change in mineralogy and different organic composition yield change in the electrical potential of shale, and thus well-log results are unlikely to be applied directly to such deposits. Therefore, first a calibration of the laboratory analyses should be proven, which can affect the interpretation of the well-log data.

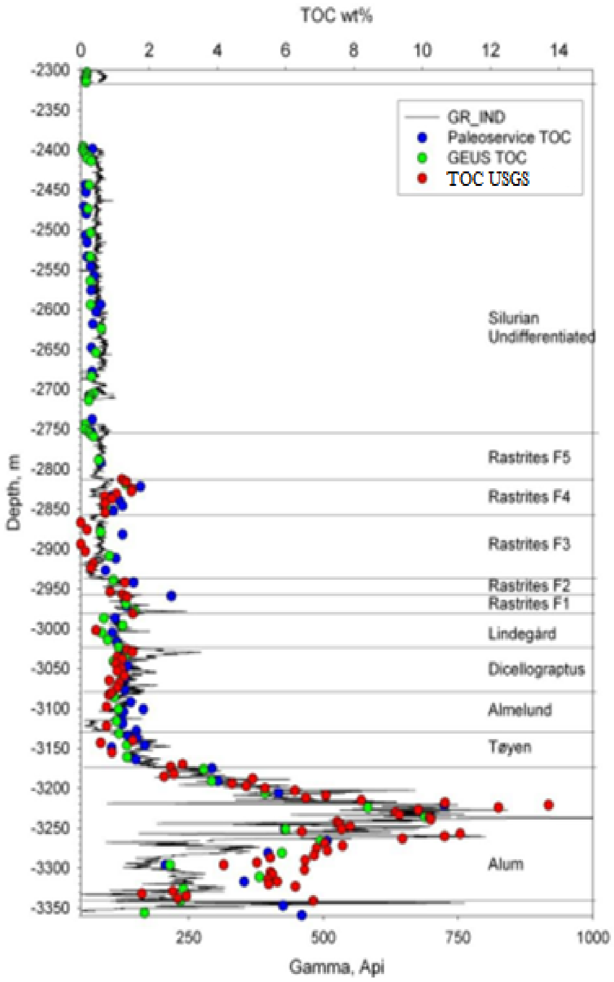
The presence of kerogen and its abundance lowers the electrical conductivity of the rock. As a part of the TOC of the formation, the kerogen can make an implausible consideration for the gas in the shale, than the real and actual gas saturation percentage. This is why Archie`s equation (9) was implemented (*Archie, 1942*), to transform resistivity logs from quality based calculation of resource in place, to quantitively expressing the in-situ resource (Equation 9). The design and variables for the equation were first directed for different than shale lithotypes, such as carbonates and sandstones, but then corrected for clays present in shale by subtraction of the proportional deflection produced by the conductivity in the rock (V_{clay} – volume percent of shale).

$$S_w^n = \frac{aR_w}{\phi^m R_t} - V_{clay} = F_r \frac{R_w}{R_t} - V_{clay} \qquad (9)$$

The equation (9) relates the pore water saturation (S_w), with the total porosity (ϕ) and the resistivity of fluids (water) in pores (R_w) to the total resistivity of the rock (R_T).Extremely high capillary pressure in pore-throat network of shale, confines water in those small void spaces, due to the physical incapability of overcoming the capillary forces, and makes the fluid immobile by keeping it inside the pores. Consequently, this will affect the resistivity log, by heightening the conductivity of the formation and a false respond will be encountered in the signature of the reservoir. Therefore, nuclear magnetic resonance (NMR) is the best way to control and correct the resistivity log, by inputting the amount of capillary pressure-bound water (*Donaldson, 2014*). For shale-gas exploration and research techniques the major suite of logging principles account for: gamma-ray, resistivity and density/neutron logs.

Gamma-Ray well logging – has the purpose to detect emitted gamma rays from shale formations, due to the accumulation of radioactive elements in the clays, such as K, Th, or Ur. The abundance of clay minerals in shale, affects greatly the signature of those beds on the logging curves, in comparison with the low deviation of the gamma log in carbonates or sandstones. This is the major well-log that characterizes the equal intensity in shale deposits, and determines the clay content. Moreover, the gamma logging technique is not constrained to only open wells, but also can be performed in cased wells no matter of the drilling mud or fluid. This type of logs are measured in units of API (0.07 µg) of radium per ton of rock. Mid-continent shale is defined with the log intensity of 100 API (*Donaldson 2014*). This recorded gamma rays` intensity derives the shale index ($I_{GR}$) used for evaluation of clay content in a certain strata or as an interbeded layers in a sandstone reservoir. The received data is incorporated in Archie`s equation for accurate evaluation of S_w, where GR_{CS} is the gamma ray intensity recorded in clean sand, GR_Z is the one recorded at the zone of interest and the GR_{SH} is the maximum gamma ray intensity in a zone of 100% shale, or a value from a core measurement.

$$I_{GR} = \frac{GR_z - GR_{cs}}{GR_{sh} - GR_{cs}}$$



By applying the outcome of the gamma logging, a differentiation of shales from conventional reservoirs can be established. Marine deposited shale contains more uranium, thus the relation of the organic matter (type II kerogen) and the radioactive component can be a crucial indicator for organic richness (*Passey et al., SPE 131350, 2010*). On the other hand, terrestrial precipitated shale beds, have lack of uranium in their clay constituents and often there is nothing in common between the kerogen (lacustrine, type III) and the uranium quantity (*Bohacs and Miskell-Gerhardt, 1998*). A sample is given with the decreasing upward TOC in a total gamma ray response log from the well Terne-1 in the Kattegat area (Denmark), aiming to potentially characterize the shale-gas prospectus of Alum Shale deposit (Figure 17). The main outcome of the identifying the shale intervals is the net thickness value, which can be implemented in some assessment methodologies for shale gas or/and oil.

Figure 17 Gamma-ray response for a 1000 m interval of the well Terne-1 in the Kattegat area. TOC quantities of up to 14% can be seen on the logging signature curve in the delineation depth of the marine deposited Alum Shale formation. A trend of diminishing quantityof clay and API can be tracked upwards within lower depths and different than Alum formations (Gautier et al., 2013, PPT, USGS website)

<u>**Resistivity log**</u> – measures the electrically conductive components in a rock. The primary conductor of electricity in rock formations is the water (brackish to saline) allowing ionic conduction. If the bulk volume of the formation is large and the water saturated pores prevail, than the resistivity of the formation will be low. Due to displacement of the water fluids, with oil-phase when in organic matter is in abundance, the resistivity is high due to the non-conductive properties of hydrocarbons. Clay conductivity can also affect the resistivity logs, depending on the bulk volume water, porosity and pores with water saturation (S_w). Some other minerals (i.e. pyrite) are also present in shale-gas reservoirs (due to reducing conditions that enhanced organic matter preservation), which can diminish the resistivity signature of shales if their quantity is substantial. Otherwise, the high resistivity response in the rich TOC intervals of shale remains no matter of pyrite quantity. A component may represent different volumes in the shale, because of dissimilarities in its matrix density structure. For example, low density OM that is around 10 wt% TOC could correspond to 20 volume percents kerogen, whilst the high density of pyrite allows the mineral to have lesser volume, even though the high weight percentage (e.g. 10 wt% may correspond to 7 volume %) (Anderson et al. 2008).

In another aspect, shales with high maturity levels (>>3%Ro), show smaller resistivity responses in the overall rock signature with several orders lower than the ones observed in the same deposit with $R_o\%$ = 1-3. This is explained to be, because of the recrystalizing of organic carbon in graphite, which is a conductor, and is likely to occur in those thermal maturities (Passey et al., SPE 131350, 2010).

<u>**Density/Neutron Log**</u> – Density log is based on gamma rays emitted by a source that is set towards the formation and aims to record the gamma rays absorbed in the formation`s matrix and the arriving ones back in two fix distances. The bulk density of the deposit is the sum of the pore fluid density and the mean value of the matrix, which is depicted on

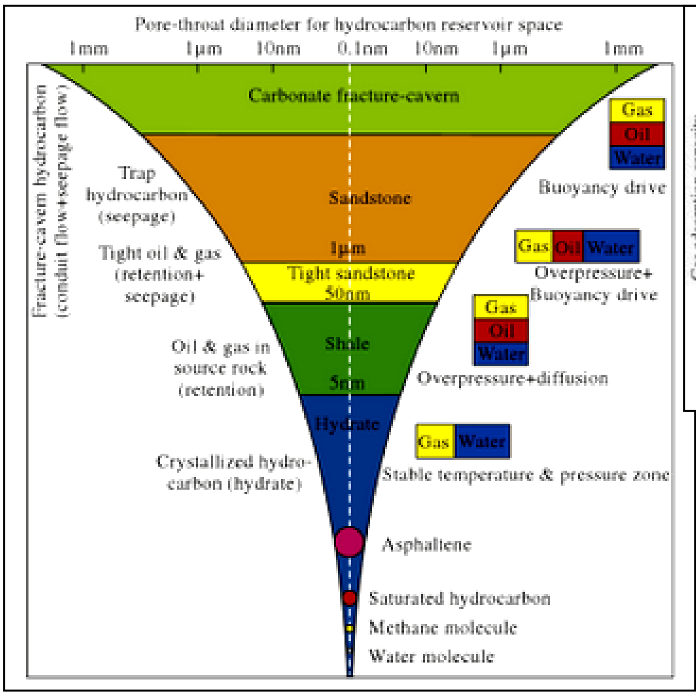
the log as g/cm³. This log yields the value for the porosity, by using matrix bulk density (ρ_b) measured from core samples. Usually kerogen`s low grain density and the abundant presence of organic matter can affect the bulk density of the shale formation substantially (Passey et al., 1990).

As a conclusion, one can infer that the initial phase of characterization of shale gas formations, comprise:

- Delineating the area , thickness and depth of the shale using surface seismic survey
- Drill a borehole, from which samples of the shale zone of interest can be acquired for analyses of the mineralogy, VRo%, porosity, S_w, TOC, formation water composition (salinity), gas saturation and composition, Young`s modulus and Poisson`s ratio.
- Well logging is executed, including resistivity log, acoustic (sonic) travel time, TOC and porosity recognition, gamma log, caliper, neutron and pulsed neutron, and NMR
- Synchronize the laboratory derived numbers with the well-logs interpretation
- Conduct calculations for resource in-place and compute algorithms and imaging to select intervals of interest and ones for completion stages

3. Nano pore-throat system in shale gas reservoirs

Sizes of 100 nm dominate in shale reservoirs which may affect the mechanism of accumulation. Some 60% of the pore throats are typically even smaller in size than the micropores, and can even block the gas or oil molecules with their 40 nm in average (slip flow), which equals in size only 40 CH_4 molecules (diameter of single methane molecule is 0.38 nm) (Figure 18) (*Cainengzou et al. 2013*). This may cause deviation from the Darcy law (pressure-driven volume flow) in the fluid transport within the micro-fractures and macro-pores of the shale. Except the nano- and micropores in the shale matrix, also meso-, macro- and natural fracture pores exist. The diameter for some of the micropores may be on average 1 micrometer. In the macro-scale and natural fractures pores the hydraulic induced fluid transport mechanism prevails, and the flow tends to turbulent non-Darcy, due to high in-situ pressure gradients. These regimes within the producing well are very complicated and cannot be modeled in the simple manner and term.



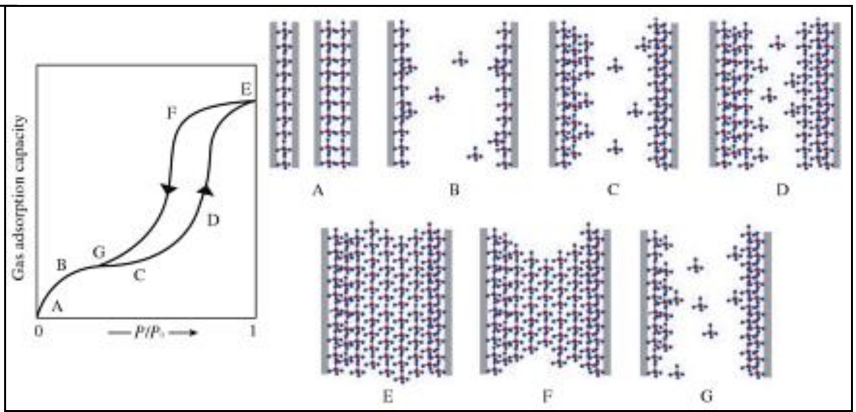


Figure 18 Comparison of accumulation mechanisms of conventional and unconventional hydrocarbons (left) and adsorption, condensation and hysteresis model of methane in micro- and mesopores – where A-D is the adsorbed state, E-F full saturation and condensation, and between F and G is the hysteresis (desorption) depending on the relative pressure of the shale reservoir (P/Po) (Cainengzou et al., 2013, Unconventional Petroleum Resources, Book)

Adsorbing isotherm data can be useful for calculating desorption capacity and gas adsorption evaluation (Figure (18) (right). Following the graph (Figure 18 right), under very low relative pressure (P/Po <0.01), micropores (less than 2 nm) in shale will have fully saturated adsorbed state (Point A), while in mesopores (2 nm – 50 nm) the methane molecules will arrange as one-layer adhesion (Point B) (*Cainengzou et al. 2013*). The increase of formation pressure constitutes for increase in the quantity of gas adsorbed in the mesopores, resulting in double-layered structure (Point C), until the pores are fully saturated with further pressure increase (Point E). The level of maximum methane adsorbing amount, is depicted in Point E, which will be also the initial stage for condensation of the sorbed gas (Point

F), when also the system pressure drops gradually (Caineng Zou et al. 2013). The hysteresis phenomenon occurs when further decrease in system pressure takes place and the drop in gas-adsorbing amount (Point F and Point G) (*Kondo et al., 2001*). The variety and distribution of pore sizes in a typical continuous reservoir, has the function of regulating the formation of hydrocarbon resources (Figure 18 (left).Fluid regimes correspond to different pore size, such as:

- In millimeter-sized pores or larger the fluids flow follow Darcy`s law;
- In micrometer-sized pores (pore-throat diameter from 1mm and 1μm) the capillary resistance force is determinable for the fluid flow path (Table 4);
- In nanometer-sized pores (size less than 1μm) the fluid flow is retained in the porous medium, because of high viscous and molecular forces between the fluids and the ambient pore environment. Fluids can diffuse only on molecular level, despite the different termobaric condition associated with siliceous sandstone, clay and shale.

Table 4 Characteristics of conventional pore-throat systems, and nanometer pore-throat ((Cainengzou et al., 2013, Unconventional Petroleum Resources, Book))

Parameter	Conventional pore throats		Unconventional pore type
Type of pores	Macropore throats	Micropore throats	Nanometer-scale pore throats
Diameter	> 1mm	> 1 μm – 1mm	< 1 μm
Porosity Type	Primary and secondary ϕ	Primary and secondary porosity	Primary and secondary porosity
Percolation mechanism	Darcy law	Darcy law	Non-Darcy law
Occurrence	Inter- and intragranular pores	Intragranular pores	Inter-crystal, intragranular pores, OM pores
Oil and gas occurrence	Free gas	Free gas dominates, absorbed gas	Absorbed gas dominates
Pore-throat connectivity	Good	Moderate	Moderate-poor
Pore-throat shape	Regular, stripped	Irregular	Oval, triangular, irregular
Surface area	Small	———	Large, maximum of 200 m^2/g
Porosity (%)	12-30	———	3-12
In-situ permeability (mD)	> 0.1	———	< 0.1
Capillary pressure	None	Low	High
Observation technology	Naked eye, hand lens	Microscope, SEM	SEM, nano-CT

Hydrocarbon migration in millimeter-sized pore spaces follows Archimedes's law and the buoyancy driven medium (*Guo et al., 1998*) calculated by Equation (10). The dynamic equilibrium (Equation (11)) represents the flow pattern in larger pore-throat channels, where hydrocarbons are driven by overpressure resulting from source rock generation. In smaller nano-meter pores it obeys the Fick`s law (Equitation (12)), and diffusion driven set-up (*Hao et al., 1995*).

$$\Delta p = (\rho_w - \rho_h) h_h g \tag{10}$$

$$p_{gf} = p_c + \rho_g g h_g + p_f \tag{11}$$

$$-D \frac{\partial^2 C}{\partial z^2} + \frac{\partial C}{\partial t} = 0 \tag{12}$$

Where Δp is buoyancy force of gas column per unit area, Pa; h_h is the height of the hydrocarbon column, m; g is acceleration of gravity, taking 9, 81 m/s^2; ρ_w is formation water density, kg/m^3; ρ_h is hydrocarbon density, kg/m^3; p_{gf} is pressure of natural gas in free phase (injection pressure of reservoir), 105 Pa; p_c is capillary pressure of overlying reservoirs, 105 Pa; h_g height of the natural gas column, m; ρ_g is natural gas density, kg/m^3; p_f is formation water pressure of overlying reservoirs, 105 Pa; *D* is diffusion coefficient of natural gas in tight reservoir bodies m^2/s; *C* is natural gas content in tight reservoir bodies, m^3/m^3; t is diffusion time, s; and *z* is diffusion distance of natural gas in tight reservoir bodies, m.

Unconventional gas found in shale deposits occurs in interparticle pores or fractures, or is absorbed on the surface of the organic matter (OM). The free, absorbed and dispersed gases are having different saturation percentages laterally and vertically in the shale formation. Once a multi-fracking productivity scheme is applied to a well, all types of gases are migrating towards the wellbore because of lower pressure than the formation pressure. Then the free gas in fractures and the nearby matrix pores become mobile. With decreasing of the formation pressure, the absorbed gas starts to desorb from minerals or OM surfaces and is triggered into the fractured system by molecular diffusion. The "mixed" gas is percolating in the wellbore, which eventually is pumped to the surface or the wellhead.

Pore-throat systems can highly affect the storage space for hydrocarbons in continuous shale deposits. The size, type and packing of the pores in the system could give a difference in calculating the gas capacity space (Ambrose *et al., 2010*) or the sealing capacity. The origin of such pore systems are related with wettability, porosity and permeability. Pore-throat diameter is 5 to 200 nm for shale gas reservoirs, 30 to 400 nm for shale oil reservoirs, 40 to 500 nm for limestone oil reservoirs and 50 to 900 nm for tight-sandstone oil reservoirs (Nielson, 2009) (Figure 19). Permeability can reach 10^{-4} to 10^{-8} mDarcy, thus the term is changed to connection rate, which can describe more accurate the seepage capacity of tight rocks. Those tiny pore channels create huge capillary pressure which can`t be overcome by the buoyancy forces, and results in the creation of the capillary force, that differs from the buoyancy one. The latter controls the HC migration and accumulation in shales. Accounting for the heterogenic pattern of OM in the intergranular storage space, when calculating the gas-in-place reserves and understanding the pore-throat systems of unconventional reservoirs, is the major step towards precise assessment of resources.

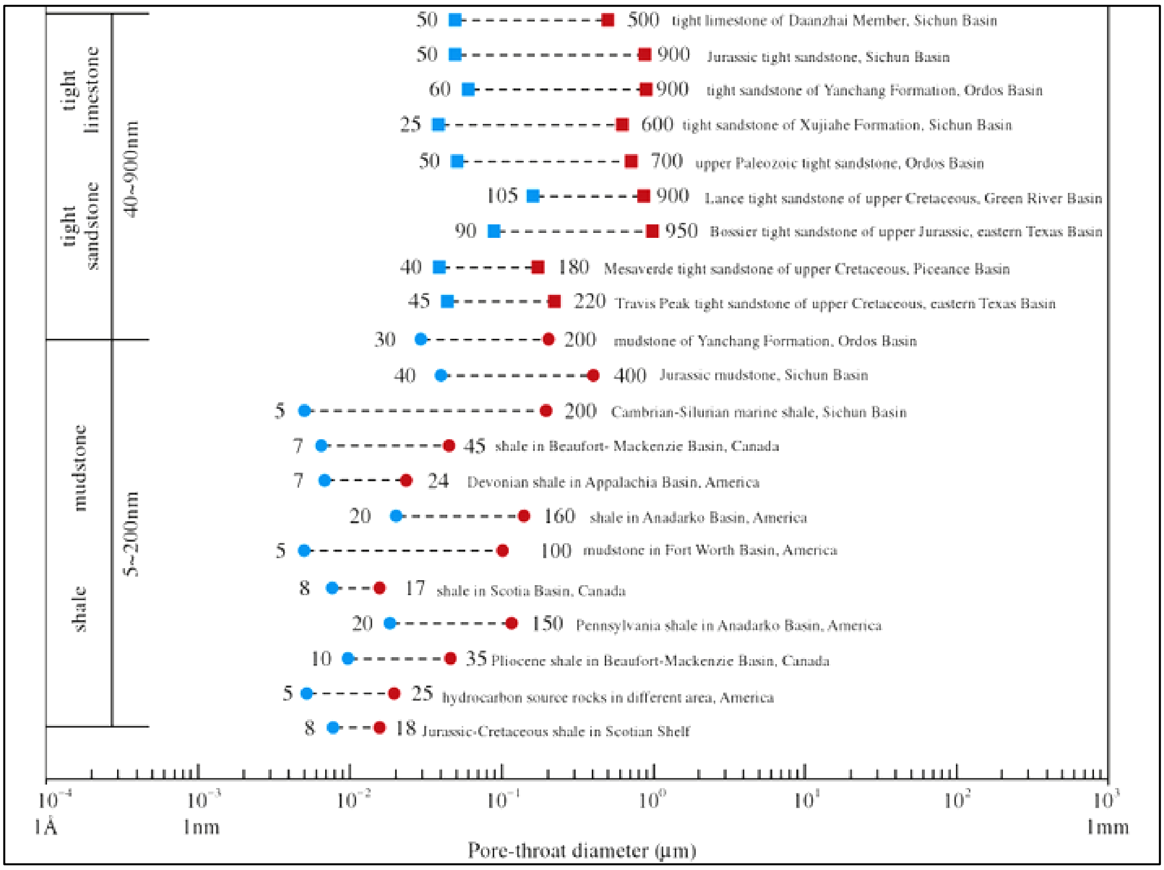


Figure 19 Nanometer pore-throats of some continuous reservoirs ((Cainengzou et al., 2013, Unconventional Petroleum Resources, Book)

3.1. Pore types classification categories

There are different classifications and divisions for the pore types which relate the pores to the properties of the reservoir. Here are some types accordingly to different authors:

- (1) Elongated pores between similar clay sheets (<100nm); (2) Crescent-shaped pores in saddle reefs of folded clay sheets (100 nm to 1 micrometer); (3) jagged pores surrounding clast grains – Debois et al. (2009);
- Phyllosilicates and (4) Organophyllic pore systems, when the Eagle Ford Formation was studied by Curtis et al. (2010);
- Interparticle pores, intraparticle pores, and organic matter pores (OM) divided by Loucks et al. (2010)
- Spongy pores and (5) pendular pores, set by Joel and Steven (2011)

For this study the classification of Loucks et al. (2010) is described and used:

Interparticle pores include intergranular and intercrystal pores. Primary and secondary origin pores are common in conventional clastic reservoirs or in tight sandstones. For shale and mudstone reservoirs, such pores are inserted in clay and organic matter`s materials, and may have inorganic clastic constituents such as quartz and feldspars. That is why the pores are less likely to be encountered as a separate interparticle pores, even though some residual ones can coexist between mineral grains and crystals. Scanning Electron Microscopy (SEM) analysis from this study indicated that interparticle pores are important as site hydrocarbon storage places (Figure 20). The grains can range from peloids, micritic grains, clay flocculates, and can be soft and ductile to hard and rigid (quartz, authigenic pyrite and skeletal materials).

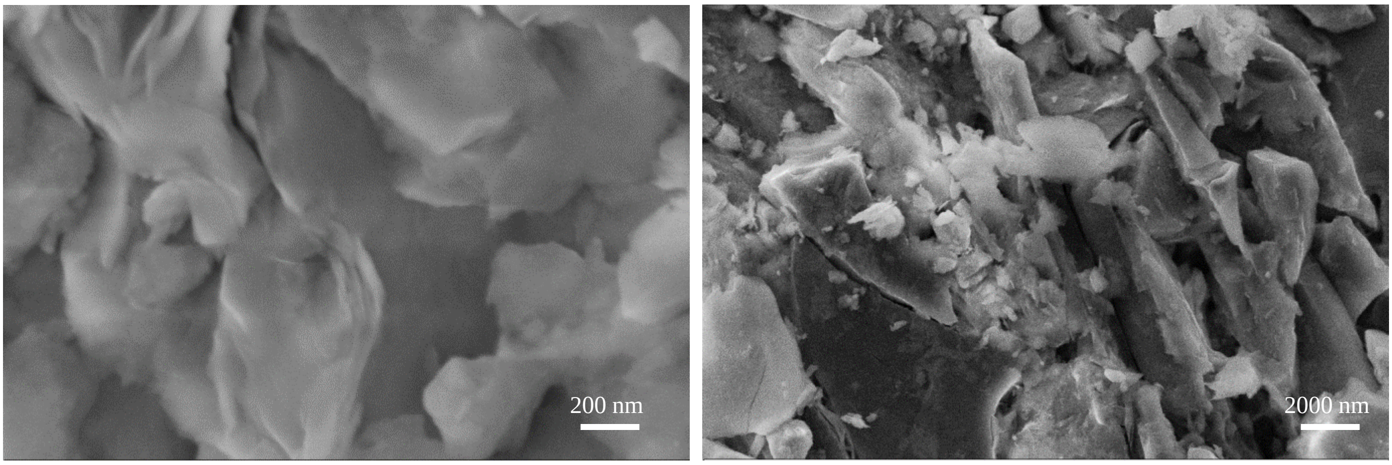


Figure 20 Nanometer-sized pore throats in the unconventional shale/siltstone reservoirs of N Bulgaria (100 nm) indicating cleavage interpores in vitrinite (right) and intragranular moldic pores in clay crystals (60 nm) (left) (SEM own observation sample BG1-J1)

Intraparticle pores are the result of dissolution of minerals during burial, where they may become unstable and recrystalise or dissolve. The diameter of dissolution intrafeldspar pores is around 50~300 nm. In clay minerals (such as chlorite, illite/smectite mixture) the pores have parallel stretched shapes with diameter of 50~720 nm. Examples of such pores are – intrafossils, intercrystalline pores within pyrite framboids, cleavage plane pores in mica and clay mineral grains, etc.

Organic matter pores (OM pores) are the most important kind of pore types in the shale reservoir. When maturity in shale increases to the oil/gas window, the expulsion of oil can lead to formation of pores in the OM. The shapes can vary from circular, oval to net-shaped. Diameter of the pores is ranges from 5 to 650 nm, with average value of 150 nm. They require thermal maturation level of >0.6% R_o to develop organic matter pores, i.e. the beginning of oil generation (*Dow 1977*). Porosity in a single organic matter particle ranges from 0 to 40% (*Loucks et al., 2012*).

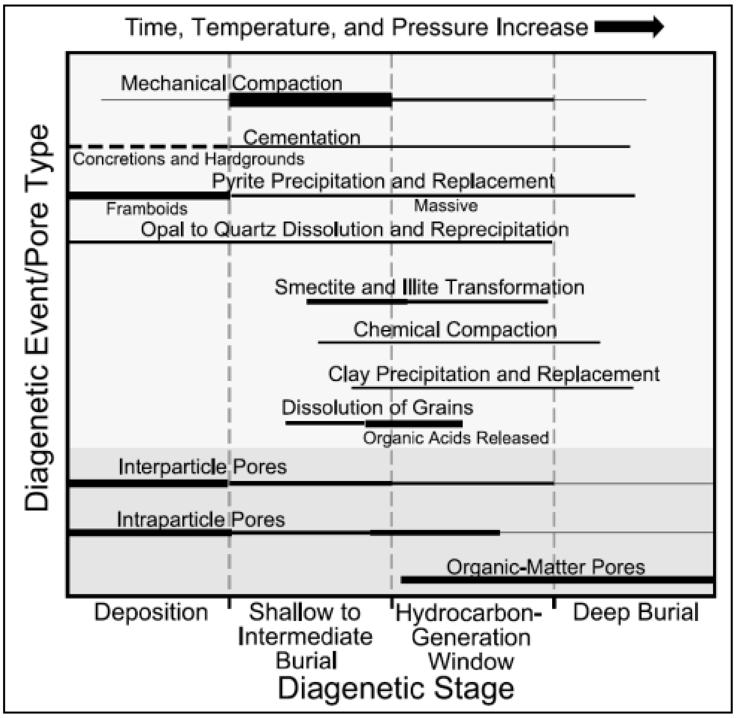
Besides talking about nano-meter pore throat systems, in the oil and gas industry a new term called "nano-hydrocarbons" was proposed (*Cainengzou et al. 2013*). This concept is assumed to be the future direction of petroleum industry. The term depicts the accumulated hydrocarbons in a storage system within nanometer-sized pore throats in shale gas and tight oil deposits, and is researched through nano-technology.

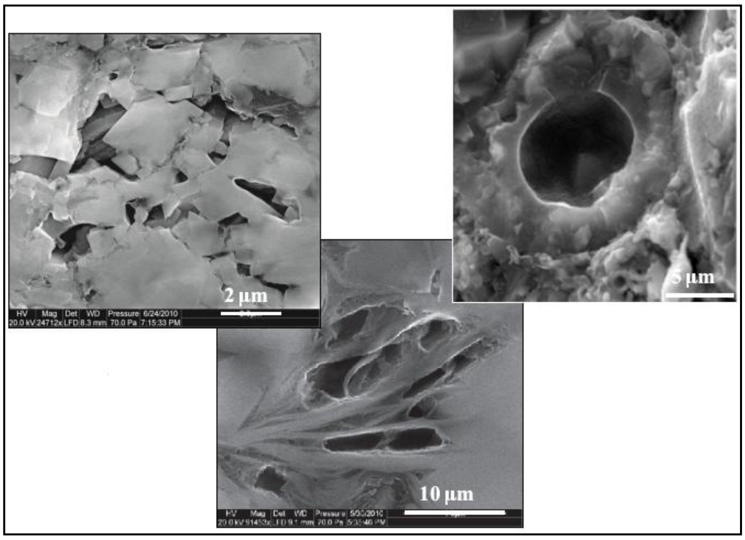
In the spectrum of fine-grained reservoir rocks most of the shale deposits that yield gas have a "porous shale" system type. That means that the source rock has significant inter/intra-grain porosity at oil to gas/condensate level of maturity. The secondary migration is absent or minimal, while the natural fracture permeability is named for the dominant or distinctive component. Shale gas plays with such properties are situated in the United States, namely: Eagle Ford, Haynesville, Woodford and Wolfcamp.

The interparticle pores (between crystals) are more likely to be interconnected than the intraparticles (in the minerals and OM).The OM pores, show connectivity only when the bulk organic matter is abundant (high TOC) (Donaldson, 2012).Furthermore, the influence of the diagenesis on the pore system is a major factor affecting the capacity or volume of void space in the reservoir rock during later generation processes. Compaction is a severe destructor of interparticle and intraparticle pores, especially in ductile grain-rich mudrocks. It can decrease the pore volume up to

88% with several kilometers of burial thickness (*Loucks, 2012*). On the contrary, hydrocarbon generation can yield OM pores in the kerogen during thermal maturation even in deep intervals (Figure 21).

Figure 21 Diagenetic effects on pore-throat systems in unconventional shale reservoirs (left) and intra- and intergranular pores (right) (SPE, File 131768, ILC-Tab, 2013)





Unconventional oil and gas reservoirs and their accumulation patterns are more affected by diffusion, than from regional hydrodynamics like in conventional reservoirs. Although segregation between the fluids in continuous reservoirs is not obvious, it does still occur in hydrocarbon migration effect around the sweet spots. The oil, water and gas coexistence is complicated in those reservoirs with different saturation levels for the HC elements. The forces that characterize the boundaries of a shale gas or oil reservoir are in principle two: <u>the driving force (reservoir forming) and the resistive force.</u> The driving force is affected by hydrocarbon generation stress, under compaction and tectonic intensity; whereas the resistive force is present due to capillary forces and pore pressure (*Cainengzou et al. 2013*).

3.2. Matrix permeability and flow patterns in shale

Even if the gas in place resources (GIP) for shale and mudstone reservoirs are considerably high, economic production rates are technically difficult to achieve, due to lack of information and researches for the fluid transport processes in the matrix and fracture systems of the lithotypes (*Amann-Hildenbrand et al., 2012*). The fluid flow in fine-grained sedimentary rocks is affected by the type of pore network system, permeating fluid, formation pressure and effective stress. The complex shale reservoirs, encounter different flow regimes in their pore systems, depending on the size and distribution of the pores. Controllers of the flow patterns in such rocks are a combination of desorption and diffusion phenomena within the micropores and Darcy flow in the macro-pores, micro fractures and fractured network system (*Gasparik et al., 2013*). The mesopores are commonly considered as a mixed fluid system with the appearance of both – Darcy flow and diffusion mechanism (*Chalmers et al., 2012*). In the shale matrix, the gas diffusion is affected by partial pressure of the gas phase, the throat diameters and pore size distribution. Pressure-driven flow (Darcy flow) is highly affected by the concentration and saturation of water and other fluid phases, because of capillary forces acting with both hydrocarbon and water phase systems. This leads to triggering of the Darcy flow fluid regime of the hydrocarbon phase (which partly consists of wetting fluids) only when the capillary entry pressure is exceeded (*Schloemer and Kross, 1997*). Further factors acting on the capillary entry pressures in shale reservoirs are throat diameter, gas-water interfacial tension, and wettability.

Natural and secondary (artificial) fractures are considered as main pathways for producing gas from commercial shale prospective, due to low values of the permeability in shale/mudstone reservoirs. Previous studies found out that even if natural fractures are enhanced to a certain level, with the starting of production, the phenomenon of limiting the long-term gas flow rates is due to the matrix transport system (*Swami and Settary, 2012*). The information regarding the matrix characteristics of organic-rich shales is scarce, and still less is known or investigated for the fluid flow. Parallel coexisting of different flow regimes in the shale formations is the main reason for grouping the different fluid transport systems in correspondence to their natural pore space occurrence. The natural, secondary (hydraulic-fractures), micro-fractures, and bulk matrix volume within the shale, tend to have different time and length scales of transport characteristics. The main types of flows accordingly to their pore distribution presence (Amann-Hildenbrand, 2012):

- Turbulent non-Darcy flow in hydraulic fractures – high local pressure gradients in shale deposits lead to initializing of non-Darcy flow patterns with turbulent macroscopic kinematics. The high pressure difference helps the acceleration of the flow and heightens the velocity of the gas/water mixture in the reservoir void spaces. And because source rocks, are deeply buried (shale with thermogenic gas), they are mainly with overpressure specifications and immobile HC.
- Darcy flow in micro-fractures and macro-pores – Darcy flow is known to be the main regime associated with fluid transport within the microfractures and macropores of shale/mudstone rocks. The mathematical expression of the Darcy`s law, describes the proportionality between the velocity of the flow to the pressure difference exerted in the reservoir. Even though, Darcy`s law implies wide variety of considerations, and is valid for most of the pore-throat flow velocities, it cannot be implemented when it comes to gas/water transport regimes in micro- and meso-pore throats.
- Slip flow in macro-, meso- and micro-pores – also known as Klinkenberg phenomenon is a non-Darcy effect governed from turbulent (non-laminar) regime of vapor flows in porous media. The slip flow occurs when the average size of the pore throats equalizes with the size of the gas molecules (free path pattern), which cause the velocity of the molecules to increase (slip) when a contact with the walls of the pore is encountered (*Klinkenberg, 1941; Soeder, 1988*). The phenomenon is thus located mainly in fine-grained sediment matrix system, which is represented by meso- and micro-pore throats. Klinkenberg documented that the apparent permeability to gas is a function of the average pore pressure. The measured gas permeability coefficients, k_{gas}, find their limit at infinite mean pore pressure, where the permeability value is referred to as the Klinkenberg-corrected permeability. In the mathematical expression of the process (Equation 13), k_∞ represents the Klinkenberg corrected permeability, which can be derived from the intercepted line on a Klinkenberg plot, of the permeability coefficients versus the pore pressure:

$$k_{gas} = k_\infty\left(1+\frac{b}{P_m}\right) = k_\infty\left(1+\frac{4c\lambda}{r}\right) \tag{13}$$

Where:

- K_{GAS} – apparent gas permeability
- b - gas slippage factor
- λ - mean free path of the gas molecules
- r – Mean pore radius
- c – Dimensionless constant

- Diffusion – the elongated desorption of HC molecules from the surface of the organic matter in shale, and their diffusion into the meso- and micro-pore system, is the place where this mechanism is found. Moreover diffusion occurs in the polymer matrix of the kerogen along with molecular transport. The gas levels and abundance (concentration and chemical potential gradient) are the dominant factor for the rate of diffusion within the matrix section (*Javadpour et al., 2007*) described by Fick’s law (Equation 12).

The difference in the permeability is likely to be affected by the molecule size of the fluids, gas sorption in the matrix, and slip flow phenomenon. Shale reservoirs can constitute of sub-nanoDarcy to micro-Darcy pore systems, which are highly linked with the rock`s deposition properties – moisture content, anisotropy, effective stress, permeating fluid, and salinity in the pore fluid composition.

Typically in a shale formation, the two fluids permeating through the medium can be both oil and water, or gas and water (depending on the maturity level and HC type of bearing-generation). For a gaseous phase as permeating fluid, volatility and mobility set the expansion and change rate in a volumetric flow along the transport and migration paths. For water the main form of the Darcy equation can be applied, but for the gaseous phase it is better to use the integrated form of the equation that accounts for compressible fluid flow. The Knudsen number (K_n) is a parameter needed for quantification the degree of slip flow/diffusion encountered in gas flow through nano-pore throats (*Javadpour et al., 2007*). It is expressed by the ratio of the mean gas free path (λ) and the pore throat diameter (*d*):

$$K_n = \frac{\lambda}{d} \tag{14}$$

Where λ is defined as:

$$\lambda = \frac{K_B T}{\sqrt{2\pi\delta^2 P}} \tag{15}$$

Here K_B is the Boltzmann constant (1.3805.10^{-23} J/k), T is temperature (K), P is pressure (Pa) and δ is the collision diameter of the gas molecule.

The fluid flow in a gas/water saturated matrix system in a shale reservoir can be correlated with a change in the Knudsen number. Higher Knudsen number (between 0.001 and 0.1) leads to substantial prevailing of slip flow regime, whereas the low Knudsen number ($K_n < 0.001$) constitutes for continuum flow (Gasparik, 2013). If the Knudsen number increases further, the transitional flow regime develops from slip to diffusion flow (ends at the value of K_N = 10 as diffusion).Considering the typical nano-pore throat diameters in the matrix of organic-rich shales (1 to 120 nm), the dominant gas flow regimes are expected to be the slip and transitional flow within production conditions of shale gas. Furthermore, low permeability coefficients in fine-grained sedimentary rocks, are further decreased by the moisture content after the diagenesis. Moisture simply reduces the effective cross-sectional area of pore throats and blocks the pore spaces by capillary water under effective stress (Ghanzideh et al., 2013). That is why an abrupt change in permeability can occur. Anisotropy of the bulk mineral content (quartz alternating with dehydrated clays), water saturation and wettability can cause fluctuations in the value of permeability and matrix space volume.

3.3. Correlation between reservoir properties in shale

Among the controlling factors for achieving commercial production of shale gas, are the storage space, gas capacity, and transport and migration properties along with the amount of gas present in the shales (GIP). However, the storage mechanisms and migration flow regimes are still not well understood, which alters the amount of extractable gas that can be projected preliminary. If conventional reservoirs are specified as primarily composed of compressed gas (free gas) in macropores and fractures, then in contrary, continuous petroleum accumulations such as shale reservoirs, have a dominance of sorbed gas or adsorbed hydrocarbon mechanisms (Gasparik et al. 2013). The nano-pore throat system present in shale result in high volumes of internal surface area, and thus large molecular interactions between fluids are possible to occur (Nelson, 2009). As phase (both OM and clay) consolidates by the sorption phenomenon, more available pore volume in mudstones and shale is acquired, and thus increase of storage capacity (Gasparik et al. 2013).

Recently it has been noticed, that the presence of porosity in the OM can be developed, due to maturation of kerogen (Jarvie et al., 2007). That revealed a general correlation between thermal maturity and the concentration (abundance) of pores in the organic matter (OM) (Milliken et al., 2013). Positive correlation was found between OM percentage, micropore`s volume and methane sorption capacity in organic-rich mudstone and shale, thus gas storage is governed by abundance of OM and porosity (Chalmers and Bustin, 2008). Increasing maturation leads to degradation of organic matter and molecular chain-collapsing, and thus the microporosity volume increases (Ross and Bustin, 2009). Increase in sorption capacity with maturity is significant at low pressures, and that maturation influences the shape of the adsorption isotherm, whereas the Langmuir pressure correlates inversely with maturity (Zhang, 2012). Sorption capacity measured in regard to TOC, is increasing with the order of increasing the number of the kerogen type (I<II<III), which was attributed to higher capacity of vitrinite, instead of other macerals (Chalmers and Bustin, 2008). There are either variations of sorption capacities with OM properties (TOC, kerogen type and maturation), controlled from pore distribution and sizes, or based on changes of the surface chemistry of aromatics (which changes with maturation) (Zhang et al., 2012; Bernard et al., 2012).

All those parameter variances and properties of the gas storage in fine-grained sedimentary rocks impose complex assumptions of variables, which require sufficient research data at precise conditions for further justification. Sorption capacities of shales are quite low, compared to that of coal (10 to 20% smaller), which requires optimization of the pressure-temperature ranges of the laboratory equipment, in case to fully reproduce the P/T conditions of deep shales.

In shale reservoirs in great importance are the interaction of the fluid saturation and the bulk volume of hydrocarbons. Due to differences in is investigation of S_g value, some main principles might be mistaken. If shale is composed of 5% bulk volume of gas, measurements of porosity can be different for every laboratory experiment – Sg=25% to Sg=80%. The offset and high tolerance is experienced by the different reference porosity (laboratory calibration) but fixed bulk gas volume (5%). For shale gas formations emphasize on the bulk gas portion should be directed, with less weight on the notion for porosity of the gas and water (S_g and S_w) (*Passey, 2010*). The same is true for the TOC in wt%, because it corresponds to twice more amount of volume percentage due to low density of organics (1.2 g/cm^3) (SPE, 2011).

4. Shale Gas Reservoir Volumetric data and Resources base

There are different terminologies for naming and defining the quantities of gas that is situated in a reservoir. Gas in Place (GIP), which is called Original Gas in Place (OGIP) and the Ultimately Recoverable Resources (URR) or the alternatively used Estimated Ultimate Recovery (EUR), are only some of the classifications of resources. The GIP abundance apply to the total volume of gas including the one that might not be recovered, whereas the URR is the sum of all gas expected to be recovered or produced from a sedimentary basin, play or spot. In IEA Energy Outlook 2008, one can find a summarized conceptual notation of all definitions for resources and reserves, and their partial size (reducing size from left to right):

[OGIP [URR [TRR [ERR [(IR – CP) = RR = 3P [2P [1P]]]]]]]

[Original Gas in Place [Ultimately Recoverable Resources [Technically Recoverable Resources [Economically Recoverable Resources [(Initial Reserves – Cumulative Production) = Remaining Reserves = Proved + Probable + Possible Reserves [Proved + Possible Reserves [Proved Reserves]]]]]]]

Technically Recoverable Reserves (TRR) encompass the gas recoverable with available technology, where as economical reserves (ERR) include the resource which exploitation should be profitable and economical with current technological advancement. Those were the main resources, whereas the reserves (IR, RR and 3P, 2P, 1P) are the remaining technologically and economically extractable gas and the different probability percentages (1P=90%; 2P=50%; 3P=10%) for the proven reserves, which in total comprise with a smaller number than the initial OGIP resources. Schematic depiction of the proportions of some resources and reserves are viewed in the figure below (22).

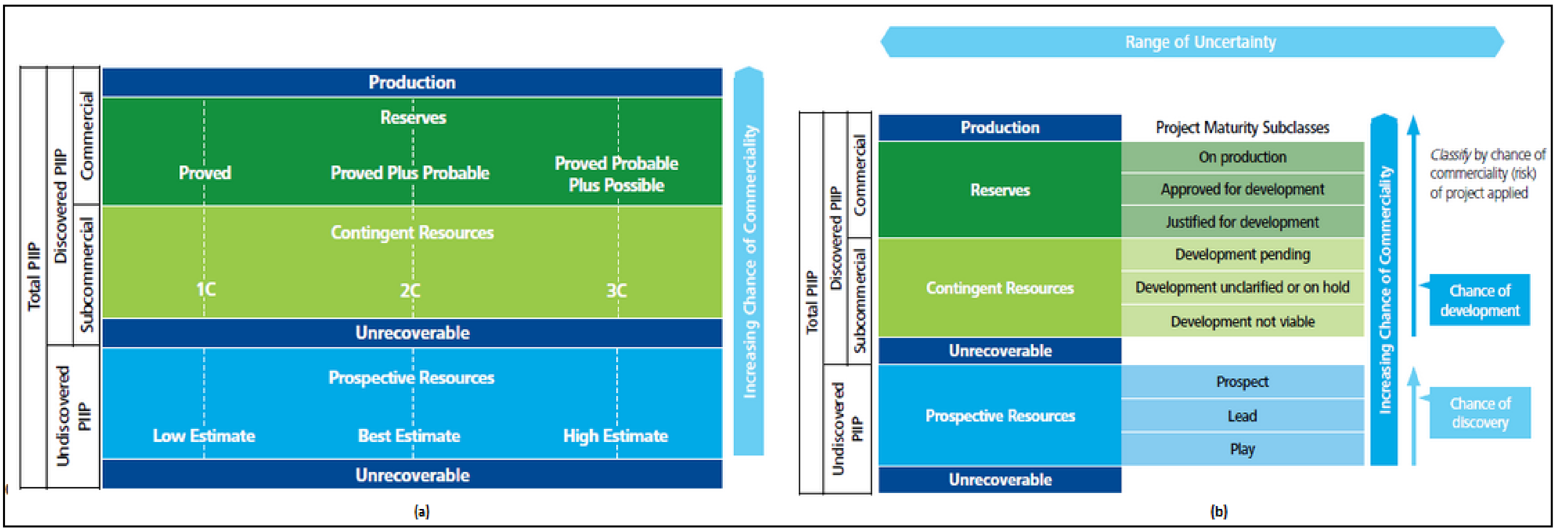


Figure 22 Petroleum resources classification framework, and proportions (SEC's Regulation S-X, the PRMS, and the Canadian Oil and Gas Evaluation Handbook)

The EUR is referred to a single well estimation of the gas potential, and is a main parameter to assess the profitability of a sweet spot. EUR helps to predict the future revenue, depletion calculations and total profit from a single well.

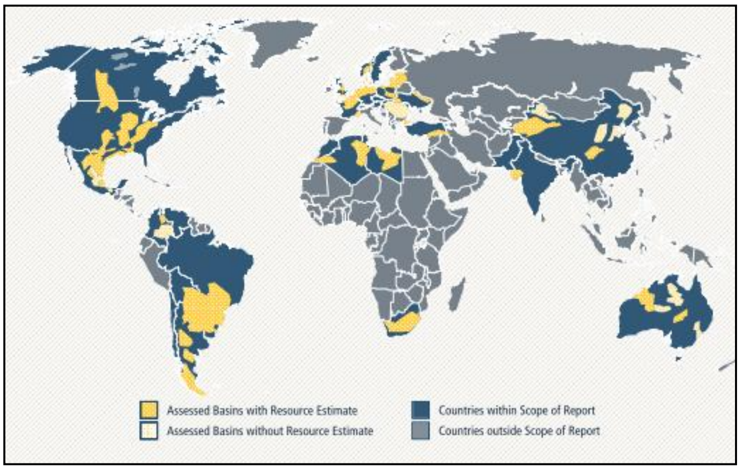
Because of slightly different flow rates within the unconventional gas deposits compared to conventional one`s, the EUR might change abruptly and cause a downfall from positive to negative values in shale gas production. Recovery rates for continuous petroleum deposits such as shale gas, CBM, tight gas are in times smaller than for conventional deposits (80%). EUR differs also on the different continents – European shale deposits seems to be less attractive than the ones in North America, which will conclude in diminished gas flow rates during production in European wells for shale gas.

To gain a better understanding of the total resources, and the ones that have been preserved after generation in the source rock and will be available for production, a loss succession must be presented. Only a fraction of the oil that is generated is produced (< 1 **‰)**, due to hydrocarbon loss during migration from an active source rocks through basin fill. The recoverable HC from commercial accumulation that are generated are minor in quantity, because of relative magnitudes of hydrocarbon loss change from case to case. After the active source rock period (HC generation), the first loss occurs with the primary migration, subsequently after the basin filling the loss to surface seepages (due to faulting and subsidence) starts, then the secondary migration loss (which is the largest loss), and finally some petroleum is lost during the developing of non-commercial accumulations. Thus, even initially gas-in place resources are negligible a quantity if one looks at the bigger picture and accounts of 60% loss of HC in the whole generation and migration process.

The indispensable information acquired from geological and drilling information during production of shale gas, is crucial to determine the value of the recovery factor. The sum between the recovery factor and the risked gas in place gives an estimate for the recoverable reserves (TRR). The risked resources (Risked GIP) are calculated by combining the mean resource value by the geological success factor (drilling an unsuccessful exploratory well). In conventional resources, the value for the recovery factor can reach 80%, but for unconventional ones it is in the range of 5-30%.

4.1. World distribution of shale gas/oil resources

Tectonics, geography and climatic conditions contribute to the deposition of organic-rich sediments found across the globe (Figure 23). Companies involved in unconventional oil and gas exploration and development are mainly focused on marine sediments that are enough thermally mature to transform kerogen into hydrocarbons. The main desirable formations for production are the marine deposited black shales, whereas lacustrine shales from shallow, freshwater deposits with terrestrial plants (which are included in the total basin numbers in the figure (Figure 23) are also targeted, but haven`t proved to be as prolific as their marine originating counterparts.



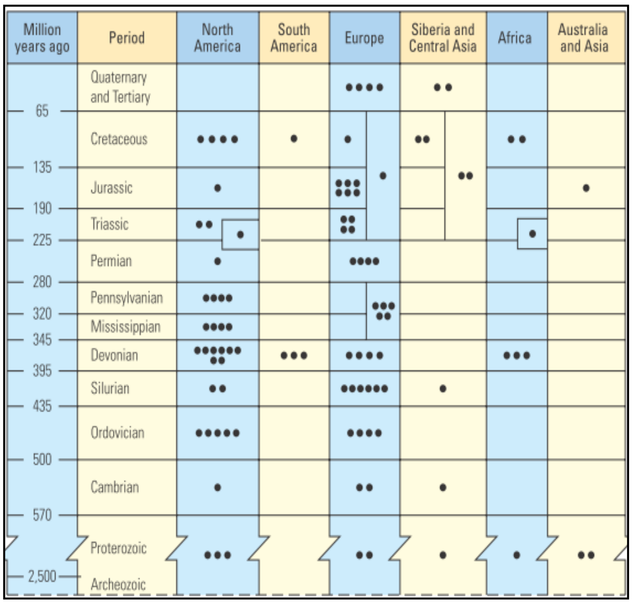


Figure 23 World map of 48 major shale gas basins in 32 different countries (left) and global distribution of organic marine shales by geologic period (right).The black circles (right) represent the number of occurrences for each age. On the world map (left) adopted from EIA, are represented all the potential shale basins, no matter of their depositional environment. (EIA,ARI, AEO2011)

In 2009, the International Energy Agency (IEA) forecasted that by 2030, a growth of 42% in the demand for fossil fuels worldwide will occur comparing to 2006. The conventional accumulations of fossil fuels are at the midlevel of development with diminished recovery factors and efficiency. Production of gas from unconventional petroleum resource has rapidly increased in the last decade, accounting for 18% of the global gas production in 2012 (EIA, 2013). After the successful boom of shale gas in North America it was realized that organic-rich shale could be a self-generating and preserving resource that can yield large quantity of oil and/or gas. Growth in production from unconventional petroleum resources, especially shale gas and tight oil, reflected in immediate development of methodologies for resource prediction, and estimation of the hydrocarbon in-place quantities. An example is the EIA`s Annual Energy Outlook (AEO2013) with the ARI estimation procedure, giving technically recoverable U.S. shale gas resources of 862 trillion cubic feet (TCF), and a total natural gas resource base of 2,543 TCF (*EIA, 2013*). The shale gas resources represent 34% of the domestic natural gas resource base in the U.S. according to AEO2013[1] and 44% in the lower 48 states onshore resources (*EIA, 2013*). The world resource was estimated to the phenomenal number of 6,622 TCF recoverable reserves (TRR) including the U.S. and 32 other countries assessed (Figure 23). Another assessment strategy for continuous petroleum resource is the United States Geological Survey (USGS) FORSPAN method, from which the agency calculated preliminary quantities of global unconventional oil resources of 3291 billion barrels (Bbbl) (*USGS, 2011*).

The volumes of reserves for unconventional resources are currently rising as new geological and drilling data is obtained all over the world during the exploration stage. Despite of their recent discovery, low development level, and the initial stage of the geological recognition, "unconventional" tend to be the future gap in non-renewable resource`s pyramid. The abrupt increase in only two years time-basis of production of unconventional oil resource accounted for a 600 million tons (MMt) additional quantities between 2008 and 2010 (Cainengzou et al. 2013), while a global volume of unconventional gas resource is set to be more than 8.3 times bigger than the conventional gas (Figure 24).

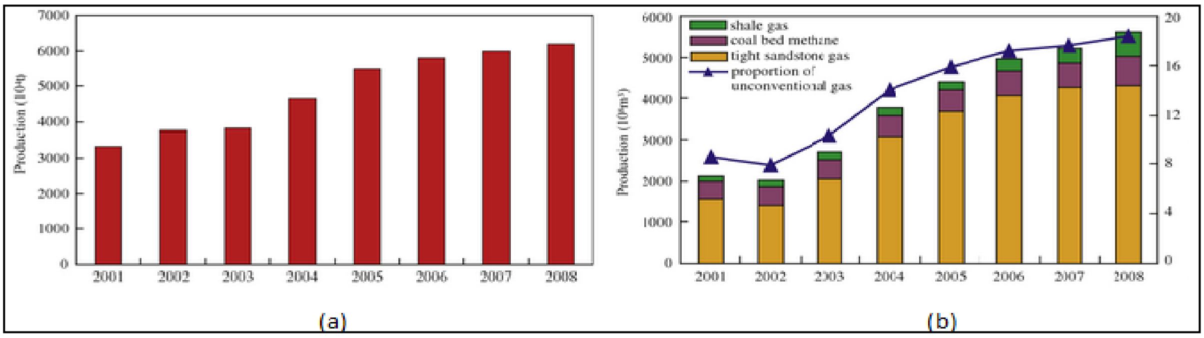


Figure 24 World unconventional oil production (a) and global gas produced from tight reservoirs (b)

Compared to the U.S. reserves of 862 TCF, the European unconventional technical petroleum resources account for around 639 TCF according to EIA[1] (2013). Most of the shale formations in Europe are in complicated sedimentary basins, which appraise for higher expenses for extraction, complex structural and stratigraphic geology. Main restriction for unlocking the shale gas in Europe is the deeper location in subsurface of the shale formations, which requires longer lateral wells to be drilled and also working in the High Pressure High Temperature (HPHT) reservoir conditions. The potential by country represents low TRR numbers for the resources in Europe (Figure 25).

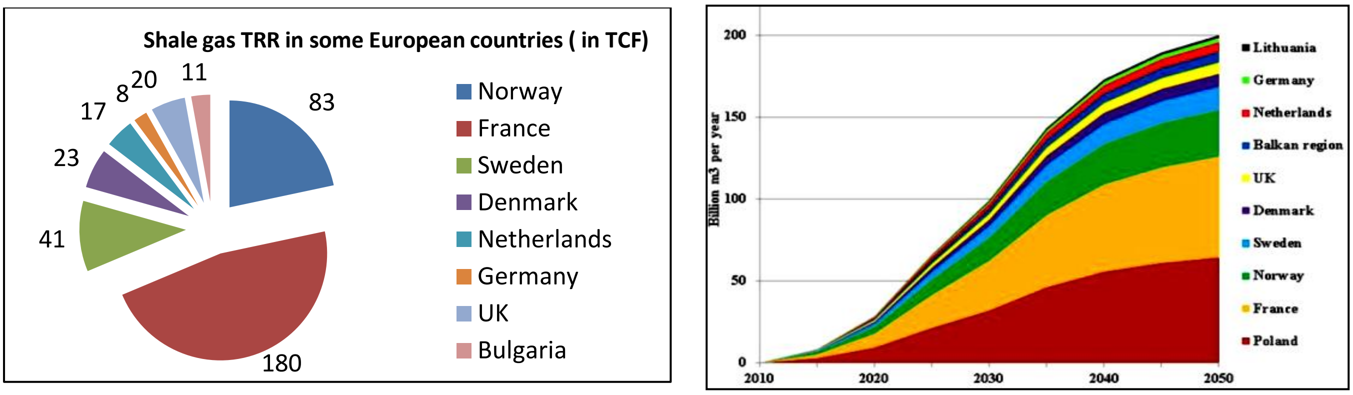


Figure 25 Distribution of recoverable shale gas reserves in some West European countries (left) and European shale gas production capacity given in BCM/year (right) (Geny, EIA, 2011)

On the both, high- and low-ends for the assessments running, there are probability factors ranging from 10% to 90% chance of recovery, selected for each shale gas or oil basin, which inputs high uncertainty levels for prospective production. For the estimation models, either conservative and long-term assessments are used (FORSPAN, Stochastic models, Spatial Volumetric Definition) with a lifespan of the projection between 20-30 years, or confined methodologies with preliminary defined boundaries and reservoir parameters based on short-term projections with the aim to reduce uncertainties (OIIP, GIIP, and Per-Well Volumetric Depletion), but adopted from conventional resource evaluations.

As the distribution of any resources on the two sides of the North Atlantic is very uneven, so is the potential of shale deposits which might yield gas-bearing HC. With the report having the primary purpose to set an average and realistic estimate for shale gas resources in some European countries, an arguable critique might be set for the large amount of recoverable reserves given by several major commissions and agencies involved in assessing oil and gas worldwide. Bear in mind that, reserves and resources as it was discussed, might prove reasonable and in-place but not economically viable and non-producible with the current technology.

The speculations of low-carbon unconventional gas, when comparing to conventional one, are still lacking confirmation. Nevertheless moratorium and petition situations in some EU countries, ARI (Advanced Resources International) points three sedimentary basins in Europe that might be in great importance for the production of unconventional resources – Alum Shale (Denmark and Sweden), Silurian Shales in Poland and Mikulkov Shale. The total resource in those basins tends to be around 1000 TCF (ARI, 2012) of which only 140 TCF are recoverable. Still this number represents very optimistic circumstances or production and policy triggering in the countries. It should be emphasized that outside North America, shale gas is not a leading but emerging field of study, and does not possess a commercial meaning because of the absent geological basin information and data for the source rock reservoirs yet, as well as higher technological costs in the production stage, due to economical factors.

An immense workflow is concentrated in the exploration activity that is undertaken with the purpose of executing and pointing the location of viable reservoirs. Examples of some international majors in the field of interest and developing of shale gas are: Canada, France, Germany, India, South Africa, Sweden, United Kingdom, Romania, New Zealand, and China.

4.3. Shale gas potential in Europe

The interplay of conditions and factors, in the U.S., created a huge momentum that led to the developing of shale gas production in the country. Such factors in North America cannot be controlled by industry, government or researchers. The U.S. approved their favorable geological conditions with the research and development stage, whereas for Europe there are still blank spots, with no geological data. The difficulties in Europe are presumed to be the densely populated area, no onshore drilling rigs on site, and geologically complex setup. As for the market situation, the U.S. at the moment are the only well integrated gas market in the world (*Makholm, 2012*), and even though Europe had some legislation packages for liberalizing gas markets in some of the countries, still there are many unknowns in this respect.

Considerations should be implemented, when speaking for shale gas in Europe, that due to lack of available petroleum industry services and number of small scale gas producers like in the U.S., it is obvious that a shale gas evolution should be expected, than a revolution stage. In countries like Bulgaria and France the lack of public supporters led to legal bans of fracking (Figure 26). The ministry of the Netherlands (the last net exporting European country, due to long history of conventional gas), decided to impose a moratorium, because of the vociferate opposition in the southern part of the country, where some exploration wells were drilled (Figure 26). Another example is the halt of Exxon Mobil operations in Poland in 2012 resulted from disappointing well data analysis, and Shell`s three drilled wells in Southern Sweden (2011), which supposedly didn`t overcome the expectations of the company, and reflected in diminished interest for shale gas exploration in the country.

As Europe`s conventional gas production is still decreasing, shale gas is set to take place as a coordinator for the dwindling production from conventional wells. The peak production period for the European Union occurred during 2005, from which point Europe increased its dependency on imported fossil fuels. During year 2010, the maximum value for consumption on the continent was reached with 48 BCF/day (*BP, 2012*). In total Europe`s indigenous production infers some 10.6 TCF in 2010, while the consumption rate had doubled to 19 TCF (*Rogers, 2011*). This makes Europe the second demanding natural gas market in the world. The domestic production decline expectations in 2020 will reach 7 TCF, and the imported natural gas value in the same year will rise with 65% in total (*Rogers, 2011*).

Figure 26 Shale gas potential in Europe (Source IEA). Bear in mind that the potential in 5 countries up to date is doubtful because they have imposed the moratorium for restricted completion stages or exploration phase (including France, Bulgaria, Luxemburg, Czech Republic and the Netherlands). In the majority of the countries, already licenses are obtained, and permits have been issued. In Denmark, Total E&P is expected to start exploration drilling in 2014 and 2015 in the northern part on Jylland. Poland has more than 112 exploratory wells already drilled on the five shale basins in the country (Report, S. I. (2005). Geology and Resources of Some World Oil-Shale Deposits Scientific Investigations Report 2005 – 5294.).

In Europe, if higher decline rates occur after some years of production as in the United States, and preliminary reserves from the assessments running are incorrect, the anticipated domestic shale gas potential and "revolution" can turn into a misleading new industry. McGlade, Speirs & Sorrell (2012) published a table "*choosing the most appropriate current estimates for shale gas*" with value for Europe of 561 TCF as their central assessment (McGlade, Speirs & Sirrek, 2012). In it, for Western European countries 508 TCF of resource calculated, whilst for Central and Eastern Europe 38 TCF are expected (*Rogner, 2009*). Not all the agencies provide a summarized median value when compared with other assessors (Figure 27), from which a confounding maze of numbers derives.

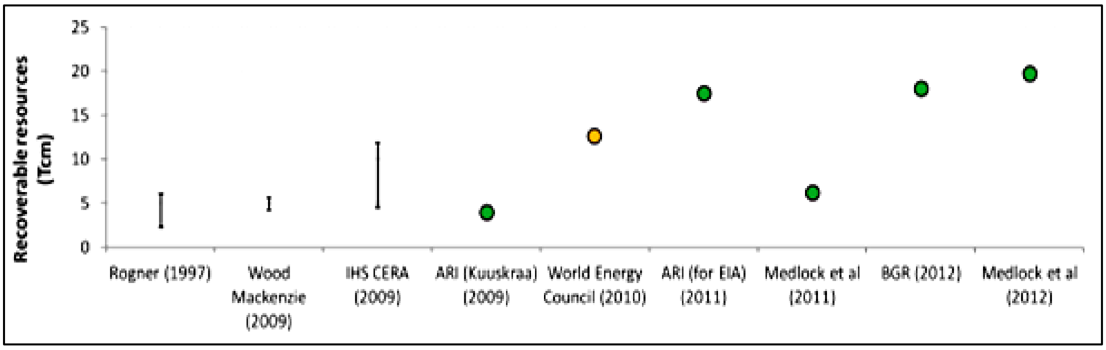


Figure 27 Estimates of TRR for shale gas in Europe – yellow point corresponds to an estimate that was stated as economically recoverable resources. The range for Rogner`s estimate is derived using a 15-40% recovery factor (Shale, W., & Resources, G. (2012)

Scandinavia`s shale gas assessment is sparser, than the Eastern European one. The high TOC, maturity level, and relatively shallow depth (1200 m in average), constitute for potential shale basins to be developed. Nevertheless, the high uranium content (*Schovsbo, 2006*), and the normal pressured reservoir (only some zones are overpressured) that could lower the evaluation resource potential, the potential of Alum Shale is large. For the Swedish parts of Alum Shale some 164 TCF of risked shale GIP and 41 TCF of TRR are estimated (*Kuuskraa, 2011*). On the other hand, Medlock (2012) the shale potential in the Danish part is 23 TCF (Figure 27), while Gautier et al, 2013 (USGS) recently introduced the new assessment for recoverable reserves of shale gas in Denmark, concluding the value of 6.9 TCF.

Poland is given a promising future for shale gas exploration, and is noted to have medium-term prospects, because of advanced drilling in the exploration phase, and "*above-ground factors are generally less of an obstacle to the development of such resource than elsewhere*" (*IEA, 2012*). The numbers show unrisked resource endowment of 710TCF and 100TCF of technically recoverable shale gas (*Vello Kuuskraa, 2009*). According to the German BGR the TRR of shale gas in Poland are 180TCF (*BGR, 2012*), which coincides with the calculations of *DERA* (187.03TCF for TRR). This gives the impression that their conclusions are based on EIA assessment (*Musialtski et al. 2013*). The estimates of 187TCF TRR (Kuuskraa et al., 2011), were reduced by the Polish Geological Institute (PGI) down to 12-27 TCF. The precise calculations given from PGI are : a maximum of 67,80 TCF of recoverable resources onshore and offshore Baltic (Podlasie-Lublin Basin) and mean value of 20TCF, which are up to 4 times higher than the conventional gas fields in the country (5.12TCF) (*PGI, 2012*). The recent estimation of 1.3TCF of potentially recoverable shale gas was made by the USGS (*Gautier et al., 2012*), which according to the author has uncertain data involved and that appropriative analogs in the assessment with U.S. basins were considered (including the EUR and drainage areas of lateral wells) (*Gautier et al., 2012*).

France and UK - France was considered to be one of the pioneer countries for shale gas production in Europe, because of the same resource base as in Poland – around 180TCF given by *DERA*. The low thickness and limited assessment unit area for the North Sea-German basin and the Paris South-East France, concedes the shales to have unfavorable characteristics (except maturity level and TOC data). The black shales in the Upper Jurassic of the South-east Basin in France were estimated by Medlock (2012) to be 62 TCF, without taking in consideration the Paris Basin (Permian-Carboniferous age).

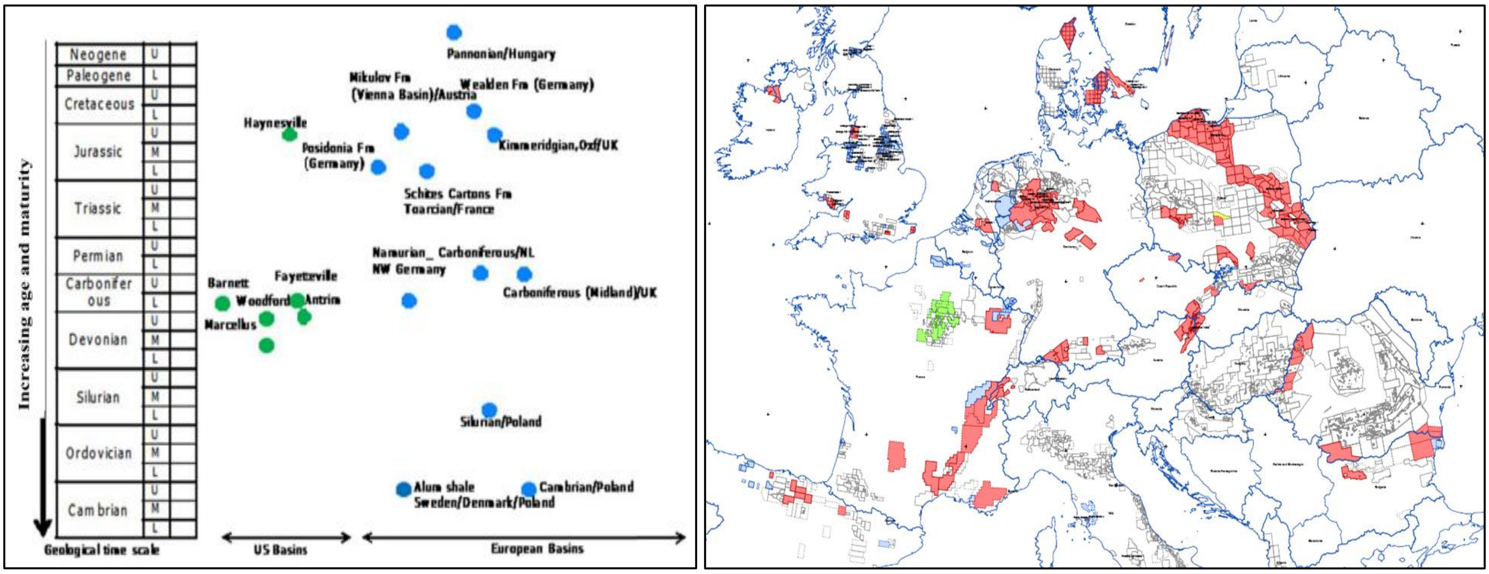


Figure 28 Unconventional shale deposits in Europe and North America by age (left) and delineation of shale basins in Europe (right) (Report, S. I. (2005). Geology and Resources of Some World Oil-Shale Deposits Scientific Investigations) Report 2005 – 5294.

The British Department of Energy and Climate Change (DECC) explains that the reserve potential in England can reach 5.3 TCF (*DECC, 2011*). The country is eager to start the production of shale gas, due to decline in conventional gas production rates, and moreover the policy of becoming self-sufficient and energy diversified producer. Therefore, it is crucial to assimilate the politicized shale gas estimations in the UK, as in many other countries (*KPMG, 2011*). The Bowland Shale situated in the Norther Petroleum System is estimated to have 19 TCF of TRR, whereas the country`s Southern Petroleum System (Liassic shales) may contain 1 TCF TRR (EIA, 2013). Summing the number the whole UK`s shale gas potential is estimated to be 20 TCF recoverable resource. Cuadrilla Resources, the only company granted with a "fracking" license in the UK, announced in 2011 that one of the two exploratory wells drilled, encountered a gas horizon and that GIP resource could turn to be 200 TCF (*Cuadrilla, 2011*).

Germany`s shale gas resources have been estimated to about 8 TCF in the large North Sea-German basin by IEA (2012), 8 TCF of TRR in the Posidonia, Namurian and Wealden shales by Kuuskraa et al. (2011).

Eastern Europe – For Romania, Hungary and Bulgaria the EIA calculates TRR of shale gas to be 19 TCF (Kuuskraa et al., 2011). For the territory of Slovakia, Hungary and Romania, the shale gas basins and areas lack of exploration data currently available for evaluation of reserves in the Carpathian-Balkanian Basin. The potential area for shale gas resource in the Czech Republic is in the south, near Austria (*Nicoletopoulos, 2012*). The Jurassic Mikulov Shale in Austria is estimated to have TRR of 30 TCF (Kuuskraa, 2009). Even though the formation ranges in the gas-prone areas from depths of 1700 m to 12000 m, it is considered as not prospective for shale gas production in the Vienna Basin (*Kuuskraa et al., 2011*).

Considering all the factors affecting the profitable exploitation of the numbers for the shale gas resource presented above, it can be pointed that some of the highlighted constrains for which the new emerging energy source can receive a skeptic start in Europe, or to be postponed for an unidentified period of time are:

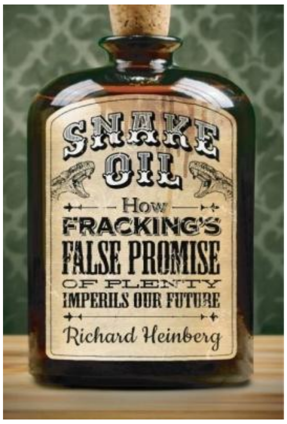
- Environmental regulations and tax incentives
- Public opinion – moratoriums and governmental policies
- Lack of geological knowledge – the status of some projects like GASH are on their initial stages
- Population density – higher than in the U.S.
- Lower competitiveness in the oil and gas industry in Europe
- Lack of employees and qualified staff to run and operate the onshore shale gas rigs
- Deeper burial of the shale deposits on the continent – up to 12 km (35 800 ft)
- Reduced scope for standardization due to heterogeneous shale deposits
- Huge infrastructure costs along with scarcer water reserves in Europe than in the U.S.
- Low individual well production cycle and long field production cycle in Europe (similarly to the U.S.)

5. The theory behind “Snake oil”

According to Wikipedia`s terminology “*snake oil*” is an “expression that originally means a fraudulent health products or unproven medicine, but has come to refer to “*any product with questionable or unverifiable quality or benefit*” (Wikipedia, 2014)[1]. Furthermore, the same source punctually defines the term “*snake oil salesman*” as: “*someone who knowingly sells fraudulent goods or who is himself or herself a fraud quack charlatan, and the like*”[1].

“Snake oil” could be found back in the Western States in North America in the 19th century, where the preparation of the “potion” has been derived from Chinese Water Snake (Enhydris Chinesis) [1]. The promotion of the preparation in the U.S. has been made by travelling salesmen, who used accomplices to the clients to proclaim the benefits of the fluid (Wikipedia, 2014)[1]. Another source (*Dr. William S. Haubrich*) in his book “Medical Meanings” (1997) claims that the name derived from the Eastern United States. Native Americans in this region would take oil from the oil seeps that naturally were expelled to ground level by faults in the lithosphere, and rub cuts and scrapes with it on their body. European settlers took advantage of that activity, and started to preserve the substance in bottles, which afterwards was sold as a “*cure for all*” (Wikipedia, 2014). The preparation was sold as “Seneca oil” (after local tribes), but Haubrich asserts that “*through mispronunciations*” the name became “Sen-ake-a oil” leading to “*snake oil*”. What is the link one will ask, for the emerging in the 19th century term “snake oil” to the relevance of this project? It is because an author called Richard Heinberg named one of his recent books – “*Snake Oil: How Fracking`s False promise of Plenty Imperils Our Future*“, which was published in 2013. The book[1] casts a critical eye on the petroleum industry hype that has overtaken U.S. energy conversation. The hydraulic fracturing during shale gas completion stages is reviewed both from environmental and economical perspectives with backed-up arguments for sufficient and rigid data analyzed from shale gas and oil drilling activities. Heinberg follows David Hughes`s book “*Drill Baby Drill*”[1](2012), that encompasses enormous quantity of interpreted drilling data from several shale basins in the U.S. The author emphasizes, whether shale gas and hydraulic fracturing is a “*cure-all miracle to North America`s energy ills, or just a costly distraction from the necessary work of reducing our fossil fuels dependence” (Heinberg, 2013)*[1].According to the author statements, the large spread of the “fracking” technology is temporarily boosting the U.S. natural gas and oil production, and “*sparked a massive environmental backlash in communities across the country*” (*Heinberg, 2013*)[1]. Thus, as Heinberg observes, that the petroleum industry is trying to sell fracking and shale gas as the best development in the energy sector for the century, with “*slick promises of American energy independence and benefits to local economies*” (Heinberg, 2013)[1].

So is “*the resemblance between “snake oil potion” and the current shale gas revolution in the U.S., and the “salesman” represented by several petroleum companies, trying to preserve the right-track of the unconventional* *fossil fuel production, real or they have nothing in common*?" (Heinberg, 2013)[1]. The book of Richard Heinberg, along with the trend of the declining rates in the shale gas/oil production in the U.S. stated by David Hughes[1], gave a basis for reevaluating or confirming some of the assessments done on the territory of North America and Europe. The various assessment agencies do show extremely different numerical results, as it was seen in this study, for their yearly outlooks and reports. Thus, supposedly, like Heinberg asserts they are: "*trying to hype the resource assessments, and by that trigger the production of the otherwise unprofitable unconventional fuel*" (Heinberg 2013)[1].In Europe at the moment thorough assessments are made in regard to the legislation framework of the Environmental Impact Assessment (EIA), included in the stages of E&P in most of the countries. The concerns of the "side effects" from hydraulic fracturing took result already with some moratoriums on the process in several countries. No commercial production of shale gas or oil has still been experienced in Europe, but only exploratory wells were drilled in some Western European countries. In the following few years, or exploration, it will be revealed whether Europe will follow North America in their progress towards shale gas/oil production.



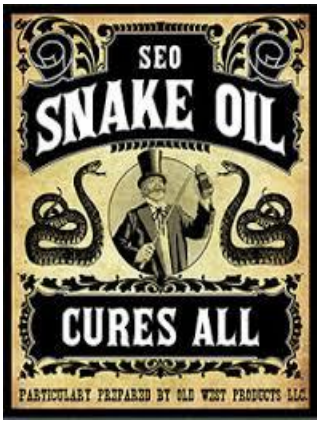


Figure 29 Front page picture of Heinberg`s book (left), and old labels for the "snake oil" products (center and right)

Conclusion

The still youthful study on the nano-pore throat systems in shale reservoirs, which is the main controlling factor for gas migration and commercial flow rates to occur, suggests that more advanced research should be focused in that area. The clustering induced-fractures in the reservoir, when the completions stage starts, provides only local enhancement of permeability values, which is not enough for securing the bulk gas to be expelled from the different pore types in the shale. Moreover, the vast lateral extension of the continuous petroleum resources makes the production rates unstable with a quick decline rate. The confounding and complex structure of the unconventional reservoirs is still not understood in total. Even though technologies like the lateral wells and hydro-fracturing made the resource accessible in North America, the control of the production and exploration processes is not handled properly until this date. The various heterogenicy of shale formations, future higher production costs, and deeper successions in Europe governs for the likelihood of uncontrolled and unsafe process in highly dense populated area. The North America`s example of declining rates between 50% to 90% in the first year is a solid prove for the tendency in the production of such unconventional resources. In addition, the recovery factor for continuous petroleum resources is less than 20%, which is four times lower than the conventional factor during production (80%). Resource and reserve base, even if they are well explained terms, have some mismatches per study with the range of deposits that are evaluated by different authors. Certain researches use "*guessing*" methods for precise description of the approach to the estimation of basins, countries or worlds shale gas potential.

It is a widespread truth that at the moment Europe shale gas production <u>tends to be Zero</u>, because of neither established flow rates rates, or boreholes (laterals) drilled with production purposes. Furthermore, the ten different continuous petroleum resource assessments for Europe (in particular shale gas) given by different authors, present inconclusive status. The values of many authors seem to be quite optimistic and heightened. The most realistic values established in the literature for the European shale gas reserves and resources tend to be the ones given by the JRC (2012) with 250 TCF, Medlock (2011) with 200TCF for the total resource and the USGS numbers for individual countries. In practice, without any drilling data established from shale deposits, <u>no one can know the exact value for the reserves in-place</u>. That is <u>the main prerequisite for the existence of wide range of estimates</u> based on indirect approach. This report will further re-calculate and investigate in the next chapter the most-realistic in-place gas resource for Denmark, and unconventional oil and gas resources in Bulgaria.

CHAPTER II – Evaluation procedures for resource assessment of shale gas/oil

6. Shale gas estimation procedures for GIP and TRR

6.1. Existing methodologies and empirical methods for unconventional resources

Conventional resource estimation and volumetric nomenclature is easily obtained, because of the confined boundaries in the petroleum reservoirs. Despite the water-table below the hydrocarbons in a reservoir, the estimations for commercial volumes of oil and gas in conventional reservoirs still remain an indirect observation and prognosis with reservoir and engineering simulation models. Furthermore, conventional HC reservoirs with their anticline trap structures (tectonic or stratigraphic traps) and precise volume area, which do not stretch laterally or vertically in large extent like the unconventional resources, are easy to evaluate. On the contrary, shale gas/oil deposits with their pervasively charged hydrocarbons, no certain oil/gas water contact and vast lateral extension, complicate the evaluation of in-place resources and their punctuate results. The vast area, with low local reserves in the reservoir, can be assessed by boreholes (core analysis), mineralogic investigation, key geochemical and geo-mechanical attributes, or logging data showed in Chapter I. Additionally in the unconventional exploration the stratigraphic cross-sections are focuses on analysis of the entire basin (compared to single or small number of facies in conventional reservoirs), with establishing the reservoir quality analysis for broad areas of the basin.

As production from continuous petroleum accumulation is growing in the U.S., and the exploration and development techniques have taken place in countries like China, Poland, Germany, and France., more attention is drawn for the study of resource assessment methods (Table 5)

Table 5 Resource assessment methods for unconventional petroleum accumulations (Caineng Zou et al. 2013)

No.	Type	Resource assessment methods in North America
1.	Tight sandstone gas	USGS FORSPAN model, estimation from single-well reserves, random simulation, statistics (estimation from discovery processes and special distribution of resources)
2.	Shale gas	USGS analogy method, estimation from single-well reserves (EIA method)
3.	CBM	Volume method, analogy
4.	Natural gas hydrate	Volume method (still uncertain resource)
5.	Oil shale	Volume method, forecasting based on special distribution of resources
6.	Oil sand deposits	Volume method
7.	Tight-Sandstone oil	Statistics analogy (estimation from discovery processes and distribution of resources)

Assessment methodologies for continuous petroleum resource involve comparative analogies, reserves estimated from single well, volume estimation, and forecasting based on the distribution of the continuous accumulations. Those methods are subsequently grouped into three parts: **1**-*analogy*, **2**-*statistics, and* **3**-*genesis methods. (USGS, 2012)*

The analogy method, with its fundamental FORSPAN model and improved simulation from USGS, is widely applied in North America. But in most of the studies elsewhere, a combination of volume method or gas-in-place method (GIP), done by EIA/ARI[1], such as in Europe is constructed. The statistical methods consist of volume reserves sequence models of sweet spots` discovery process, estimation from single-well reserves, and determination of the resource distribution by matching and forecasting.

6.1.1. Analogy method – USGS methodology

The method is cell-based, reservoir-performance model and is now considered superior, because of it computational science basis, and comprehensive integration on large scale (*USGS, 2010*). The U.S. Geological Survey divides assessed areas into:

- Region – refers to the organization unit;
- Geological province – aggregate of special units with similar geological attributes;
- Total petroleum system (TPS) – a mappable entity encompassing genetically related petroleum that occurs in seeps and accumulations (discovered or not) and generated by a pod of mature rock, with the essential descriptive geological parameters (source, reservoir, seal, and overburden rocks) that controlled the generation, migration, accumulation and preservation of petroleum;

- Assessment unit (AU) – is part of TPS and is composed of cells;
- Minimum AU (cell) – is a rectangular net in a former assessment system, or well drainage area in a new system.

Primary assessment parameters include total assessment unit area (U), percentage of the total AU area that is untested (R), % of the total AU area that is untested and has the potential to add reserves within the forecast span (S), area per cell of untested cells, having the potential to add reserves (V_i), total recovery per cell (X_i), average oil and gas ratio of untested units, and oil and gas ratio of the assessment unit. Drilling data is used for direct study and distribution of formation (reservoir) parameters (fluid saturation, thickness, permeability and porosity), and by that estimating recovery rates, determining weighting coefficients and estimating reserves (*Cainengzou et al. 2013*). If no drilling or production data is available, all the parameters have to be collected by analogy. FORSPAN method is adapted to residual resource prediction potential in developed areas. The reserves are being calculated for each cell, with the respect to the distribution of the parameters, and then the results are summarized to be the total residual source (Figure 30).

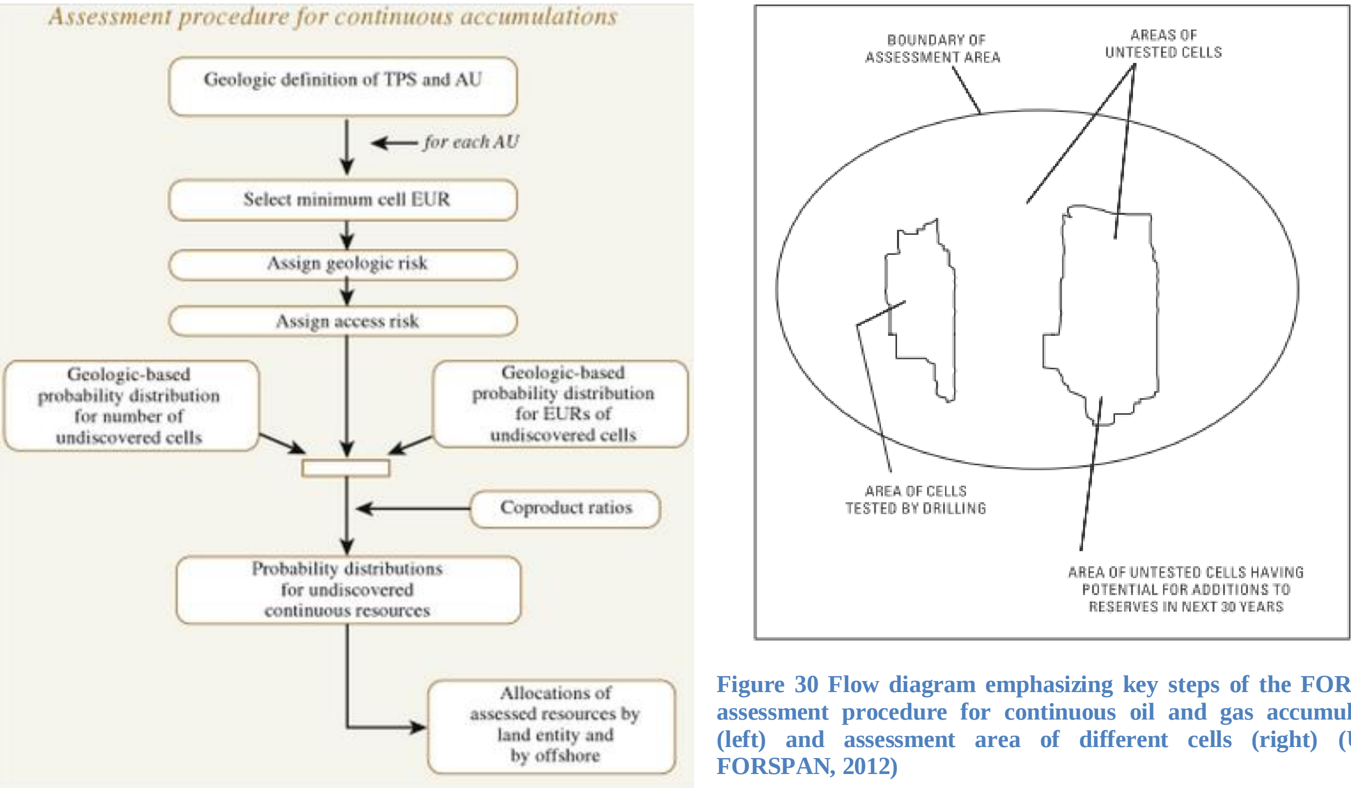


Figure 30 Flow diagram emphasizing key steps of the FORSPAN assessment procedure for continuous oil and gas accumulations (left) and assessment area of different cells (right) (USGS, FORSPAN, 2012)

In the next four steps, a brief outlook will be performed for the analogy (FORSPAN) method (*USGS 2010*):

- The % of total AU area that is untested, but has the prospect of adding resources within the forecast span (T):
$$T = R \times S$$
- Calculate the area of the ascertain AU space that is untested, with a potential to add reserves (W) :
$$W = T \times U$$
- The number of cells that are not tested and have the potential to add to reserves in the forecast (N):
$$N = V_1 + V_2 + \dots \dots + V_N$$
- Calculate the resource of the total AU area that is untested and has the potential to add reserves within the forecast span (Y):
$$Y = X_1 + X_2 + X_3 + \dots \dots + X_N$$

The explanations for the variables in the formulas can be found in the USGS digital data series DDC-69-B[1]. The method of FORSPAN was developed within the results stage, involving geological and engineering parameters that better predicted the indiscrete entities that continuous accumulations form, and narrowed the field area to better production zones (*core zones*). Such resources have abnormal formation pressure, large hydrocarbon volume in-place, low recovery factor, no dry holes, fracture permeability dependence, and they can produce immense volumes of moveable water from their fractures and cleats, and thus cannot be evaluated by conventional meanings.

The elongation of shale gas assessments for the USGS FORSPAN model has a precise threshold of 30 years. Key steps in such FORSPAN assessment plan is the estimation of the EUR for oil- or gas-prone AU, the adequate designation of generation, lithotypes, and geological timing probabilities for every cell which has a minimum EUR, and access risk definition or evaluation of probability factors for EUR of oil and gas AUs, with comparison of reservoir data and analogous area. In the estimation for oil prone AUs, the ratio of gas/oil and NGL/gas (Natural Gas Liquids), along with co-products are also included in the method. According to *USGS*[1] three fractiles (F_{100}, F_{50}, and F_0) are involved for EUR of the untested cells or an AU that can add resources. The resources can be allocated to different land units within the AUs.

A recent edition of USGS`s applied geology-based assessment estimation was published for the "Undiscovered Gas Resources in the Alum Shale, Denmark, 2013" (Gautier et al 2013), where the same methodology procedure is followed for calculating the technically recoverable reserves and undiscovered resources (6.9 TCF of gas in the Alum Shale, Gautier, 2013). The paper, that was established in collaboration with GEUS (Geological Survey of Denmark and Greenland), provides a full potential estimation for continuous petroleum deposits in the Paleozoic shales in Denmark, and thus will be a basis in combination with the next method (EIA/ARI report) [1], for implying a new calculation for the Alum Shale deposits in Denmark.

6.1.2. Stochastic simulation method for estimation of continuous resource abundance

The stochastic method is a modification of the conventional analogy method proposed by USGS (Olea et al., 2009), and solves the problems and disadvantages of the previous methods like:

- The original method does not pay attention to the EUR special relationship of different AUs units;
- The original method does not provide subtle information from existing data;
- The assessment results go against the special distribution rule (*USGS*).

The main differences between the analogy method and the random simulation (stochastic method) consist of: (1) integration in areas without wells of special link between EUR parameters and analogy with consequently multipoint simulations; (2) distribution model of parameters from geological statistics take place; (3) the new method has sufficiently small cells, which are close to the drainage controlled by single well.

6.1.3. Volumetric calculation of GIP resources for shale gas - ARI procedure

The estimation from single-well production is a classical one, introduced by ARI (Advanced Resources International), where the minimum assessment units are in the range controlled by only one well. The evaluation area is divided into small units, and based on the estimation of each unit to the resources of the whole area, which can be obtained by the formula:

$$G = \sum_{i=1}^{n} q_i \qquad (16)$$

In the equation (16), G stands for the resource of assessment area; q_i = single-well reserves*;* i = number of assessment units; n = total number of AU; and f = drilling success rate. Moreover, five crucial variables are embedded in the method, such as: sweet spot of hydrocarbon deposits, reserves of single well, success rate of drilling, boundary of the AU and minimum AU.

The methodology takes into account geological data, reservoir conditions and parameters, provided from the technical literature and internal (non-confidential) information from the authors (EIA). In case to create a robust assessment for shale gas in Denmark, partly this methodology will be viewed as fundamental for initializing the calculation.

For each assessment basin, unit and formation level, five main topics should be included and followed according to EIA/ARI report[1]:

- Preliminary geologic and reservoir characterization of shale basins and deposits (formations)
- Delineation of the areal extent of the major shale formations (gas- or oil-bearing)

- Establishing of the prospective area for each oil and gas shale formation
- Estimation of risked shale gas/oil in place (GIP and OIP)
- Calculating the technically recoverable shale gas/oil reserves (TRR)

From the reviewed methodology of ARI/EIA 2013 report[1] for shale gas/oil resource estimation, formations with unknown geophysical features, TOC<2%, total vertical depth (TVD) of less than 1000m, and greater than 5000m should be excluded when executing an assessment. The shale gas recovery rates are re-calculated using formations from the U.S. shale oil/gas plays, for analogs and geophysical parameters, and the derived result is referred to as risked oil or gas in-place and technically recoverable reserves. Even though that is not the best solution, where geologic information is absent, it is the only way to make prognoses for GIP resource. The procedure includes some subdivisions with subsequent steps:

- (**1**)Basin study and shale formations to be assessed;
- (**2**) Areal extent and gross thickness of the shale units;
- (**3**) Delineate the prospective area based on several parameters – depth, shale quality, expert judgment;
- (**4**) Estimation of GIP as a sum of free and adsorbed gas that is available in the prospective shale deposit`s area, along with OIP calculation based on oil saturation in the total pore volumes;
- (**5**) Apply a composite success factor that includes the success probability factor and prospective area success factor, which take into account the shale deposit specifications;
- (**6**) For GIP a calculation for the recovery factor by considering geological complexity, reservoir pressure, clay content, pore size, etc. is made;
- (**7**) Determine the technically recoverable resources (oil/gas that could be extracted with current technology, regardless the economic factor (cost, prices, etc.) by multiplying the risked OIP or GIP by a recovery factor (those range between 15 to 35% in the U.S. shale plays);
- (**8**) Free gas concentration (main gas in deeper shales), and adsorbed gas (adhering to the substrate) which is dominant gas for the shallower organically-rich shales.

In order to clarify each of the steps, a further detailed overview will be explained below for the EIA/ARI method (AOE2013)[1]. No certain case study will be taken as an illustration of the assessment steps, because this will be provided in Chapter III for the Danish Alum Shale.

Step 1: Conducting preliminary geologic and reservoir characterization of shale basins and formations

Geological data of the region and the reservoir (source rocks) is assembled for the shale basin and formation, with some certain specifications: depositional environment of the shale (terrestrial or marine); depth (to base and top of the shale deposit); organic-rich gross and net shale thickness; structural geology (faults and lateral extension); total organic content (TOC in weight %); and thermal maturity (vitrinite reflectance %R). This initial step, aims to acquire the first order information for situating the shale formations and basins, and filter the ones that would be prospective and will be more intensively assessed. Next a litho-stratigraphic table should be provided for the region or for the basin, along with allocation of the formations and map with an enlarged topographical overview.

Step 2: Establishing the areal extent of major shale gas formations

After having the major prospective formations (evaluation of *Step 1*), the more intensive study for the areal extent for each of them can be conducted. This can be achieved by gathering information from the technical literature for wells drilled in the area, cross-sectional figures, and other useful geological profiles. The cross-sections provide the actual horizontal extension of the deposit or identify the depth and gross interval.

Step 3: Defining the prospective area for each shale gas and shale oil formation

This step is crucial and usually the most important one, in order to achieve the volume for the proportions of the basin that are deemed to be prospective for development of shale gas. According to EIA (2013)[1] the criteria used for establishing the prospective area includes:

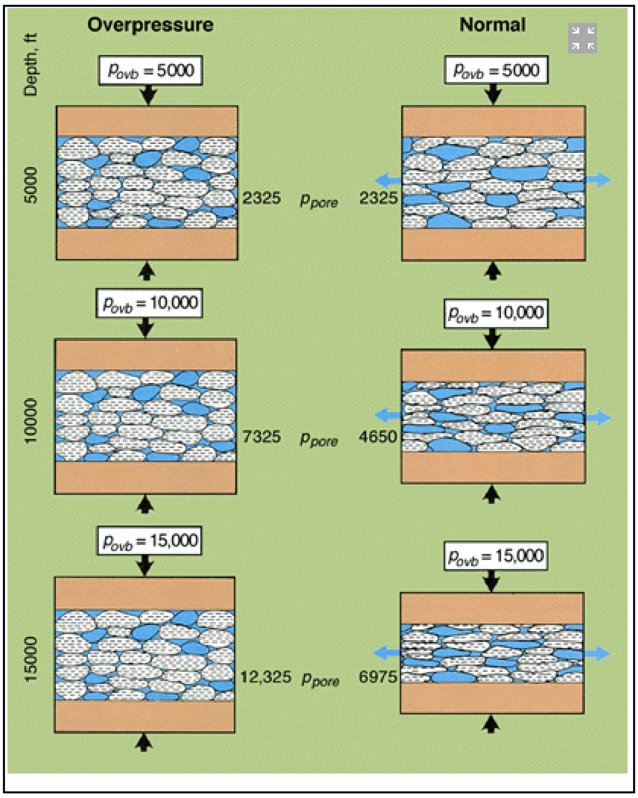
- Depositional environment – or whether the shale has a marine or non-marine origin. Shales deposited in marine environments have lower clay content, and higher quartz content, which quality sets the favorable respond and brittle mineralogy for hydraulic fracturing stimulation. Terrestrial originating shales have high clay minerals in their bulk crystalline structure, because of the lacustrine and fluvial sediment support, and thus are more ductile and unfavorable for completion activities. Ternary diagram is implemented for the specific formation.
- Depth – prospective shale should be between 1.000 m and 5.000 m (EIA/ARI, 2013).The shallower shales have low formation pressures, which will cause low recovery rates for hydrocarbons during production. In the latter, higher water content may also decrease the pore volume and the storage capacity for gas-bearing organic matter (kerogen). Shales deeper than 5.000 m are not favorable because of low values for permeability and higher production costs.
- Total organic content (TOC) – should be above 2% for prospective shale (EIA/ARI, 2013)[1].Thickness of organic-rich intervals can be evaluated from a gamma ray log. Preferably, the kerogen type for the prospective area is expected to be either I or II to ensure generating of oil and gas of the shale.
- Thermal maturity – oil prone thermal maturity prospective area has a %Ro greater than 0.7% but less than 1.0%, whereas the wet gas has a %Ro of 1.0~1.3% and dry gas greater than 1.3%. For shale gas, values or Ro% above 1.2% are favorable.
- Geographic location – even though the majority of the shale formations are offshore, the prospective area for such deposits are narrowed to the onshore portion only, in the current EIA report[1]. The prospective area includes high quality shale gas areas (which are geologically favorable), high resource concentration "core area", and some lower quality areas, which at the end leaves around 50% of the initial delineated area.
- High risk area - includes shales with complex geological properties or high clay constituents in the bulk mineralogy of the formations. To do so, the EIA/ARI report[1] excludes such cases, and delineates the resource evaluation without those regions. The modification of wells drilled in the area, and obtaining more geological information in near future, may enable the involvement the latter in the resource perspective. Better appraisal and exploration in those regions will surely change the numbers in a way from the present one.

Step 4: Estimating the risked shale gas in place (GIP)

1. Gas in-Place – the data needed for the calculation of the gas in place resources includes the areal extent, net shale thickness, adsorption isotherm calculations, density of shale and gas-filled porosity (S_g for both free and absorbed), which is governed by the P/T conditions of the reservoir, defined by the FVF (formation volume factor), and determined by the compressibility factor (z).

- Net thickness of the organic-rich shale deposit – is obtained by stratigraphic researches that mainly include the gross source rock thickness established from logging data and cross-sections. Net/Gross (N/G) ratio is calculated for the organic-rich intervals for estimating the shale with high organic content, and finally calculating the net-rich shale thickness.
- Gas in solution, and oil saturation in pore volume – if there is logging data on the appraised formation, it is used as an initial literature study for obtaining the porosity, or instead an alternative with a core sample from a nearby drilled well. If lacking of such information, the porosity percentage can be assembled by interpreting the mineral constituents in the shale along with its maturity, and then compare the results with a similar U.S. shale play or basin properties. The pores are usually assumed to be saturated with hydrocarbon fluids and water, in a different ratio.
- Pressure and Temperature – during the study, there should be a primer focus on identifying overpressured formation areas. An overpressured shale reservoir yields bigger portion of gas that will be produced if extracted, before the pressure decreases to its bubble point. The exerted pore pressure in the shale reservoir is a function of depth burial and overburden stress (Figure 31). Normal pressured and overpressured formations are presented in the figure below (Figure 31), which brings the comparison between the compaction of the lithotypes and water content in the pore space. An average hydrostatic gradient should be in the vicinity of 0.433 psi/foot (EIA/ARI) [1].The gradient is applied only when actual pressure data is not available, because water salinity data are not present in the general literature. Temperature gradient depends on the localization region of the shale deposit – whether it exerts a cold or warm geothermal gradient. An average value of the

temperature gradient is considered to be 26°C/km or 1.25°F/feet (EIA, 2013) [1] of depth, to which a surface temperature of 15.5°C or 60°F is added.



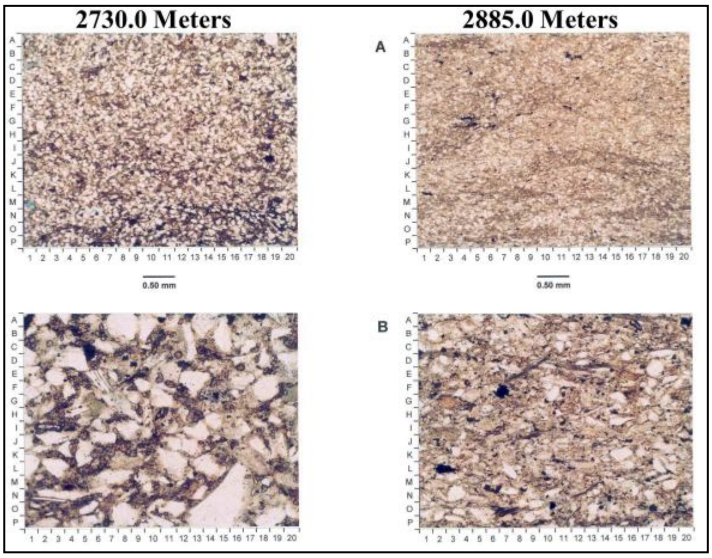


Figure 31 Compaction and burial of shales, with correlation to pore fluid loss and comparison of overpressure burial (rapid burial with poor permeability, retains the pore fluid with an ever-increasing stress), and a normal burial (with an intensive water loss). P_{ovb} stands for overburden pressure in psi and P_{pore} is for the pore pressure in *psi (left)* and pore volume reduction images of photomicrograph with increasing depth and compaction (*right*). (after SPE, File 131768, ILC-Tab, 2013)

Pressure-Volume-Temperature (PVT) reservoir data and reservoir engineering equations are used for transforming the information available and sum it into a free GIP per acre estimation (Equation 17)

$$\mathrm{GIP} = \frac{43{,}650 * A * h.\varphi(S_g)}{B_g} \qquad \text{Where:} \quad B_g = \frac{0.02829zT}{P} \tag{17}$$

- *A* – Area, in acres (conversion factor of 43.560 sq. ft. per acre and 640 acres per square mile)
- *h* – Net organically-rich shale thickness (in feet)
- ϕ – Porosity - a dimensionless fraction that is obtained from core data or logs (neutron and others) or assigned by analogy method from the U.S. shale gas basins; thermal maturity and depth can influence the porosity used for the shale
- (S_g) – Porosity with gas saturation, the porosity value is multiplied with the term (S_g) to establish the gas-filled porosity; liquids-rich shales may contain condensate and/or oil (S_o) in the pore space along with water (S_w)
- *P* - Pressure in units of *psi* - obtained from well tests information in the literature, inferred from mud weights or assigned by analog from U.S. shale gas basins; basins with overpressure are assigned pressure gradients of 0.5 to 0.6 psi per foot of depth; basins with indicated underpressure are assigned to 0.35-0.4 psi per foot of depth (EIA/ARI, 2013)[1]
- *T* – In degrees Rankin (regional temperature vs. depth gradients; the factor 460 °F is added to the reservoir temperature to provide the input value for the gas volume factor (B_G).
- B_G – is the gas volume factor, in cubic feet per standard cubic feet and includes the compressibility factor (z), which adjusts the ideal compressibility (PVT) factor to account for non-ideal PVT behavior of the gas; gas deviation factors, complex functions of P, T and gas composition, can be found in reservoir textbooks.

2. Adsorbed Gas in-place in the shale reservoirs can have a significant control on the gas storage and gas capacity. Unlike the conventional reservoirs where the main volatile fluid phase is the free gas, the shale formations that act as source rocks and reservoirs, tend to have more adsorbed gas in place (EIA, 2013)[1]. Gas adheres on the kerogen (organic matter) or some reactive minerals (like clays) in the shale.

By the available TOC (wt %) and thermal maturity a Langmuir isotherm is presented, and then Langmuir volume (V_L) and Langmuir pressure (P_L) are established. Adsorbed gas in-place is estimated using the equation (18) below (where P is the formation pressure of the shale):

$$G_C = \frac{(V_L * P)}{P_L + P} \tag{18}$$

The gas content G_C is measured in *scf/ton* of net shale, and is converted to gas concentration (adsorbed GIP per square mile) using values for the shale density (around 2.65 g/cm^3, but are highly controlled by mineralogy and OM content).

Free gas and adsorbed gas in-place are combined in the calculation of the resource concentration (Bcf or MMcf/mi^2) for the prospective area of the shale gas basin (EIA 2013)[1]:

$$GIP_{total} = GIP_{free} + GIP_{sorbed} \tag{19}$$

Generally speaking, oil in the shale gas reservoir (if any) can be in undersaturated or saturated conditions. In saturated conditions (depending on the bubble point and pressure value of the reservoir), the oil contains associated gas in solution and free gas, whereas during the undersaturated conditions, the gas is retained in the oil phase, until the bubble point is reached along the pressure difference. Some calculations need to be made for estimating the portion of the volume of associated gas in-place, which will be produced with the shale, within oil shale or shale gas formations.

3. Establishing the Success/Risk Factors – success/risk factors are used in the U.S. EIA methodology assessment for the estimation of oil in-place and gas in-place within the area of interest of the shale deposit:

- <u>Play success probability factor</u> – is the probability that at least a portion of the shale deposit will provide oil and gas at economical production rates that can be developed in future. The shale reservoirs with insufficient geologic information, and speculative production stage can have a probability play factors up to 30-40% (EIA/ARI, 2013)[1]. If some action is taken in the shale play, such as drilling of exploration wells, or further geological data is revealed in the literature, the play success probability factor is influenced and will change.
- <u>Prospective area success (risk) factor</u> – has the main purpose for relegating some sections of the prospective area to be unviable or unfavorable for production of shale gas. Areas with high geological complexity such as faults, subsidence regions, or upthrust fault blocks (e.g. like the fault-block structure of the Denmark`s Alum Shale), immature areas (R_{eq} around 0.7-0.8%) [1], and the external margins of the core areas that include shale deposits with low net organic thickness should be excluded. The factor accounts for the availability of geological data, and for the status of exploration in the area of the shale play. More strict definition of the area examined, is provided by further delineation, and thus a change in the area success risk factor. The factors (areal and play success) are then combined to derive a single <u>composite success factor</u>, with which to risk the gas in place for the assessed area (EIA/ARI 2013)[1].

<u>Step 5: Estimating the Technically Recoverable Resources</u>

Those resources are calculated by multiplying the risked gas in-place (GIP) by a shale gas/oil recovery efficiency factor. The factor includes geological parameters, mineralogical information (geo-mechanical properties for favorable artificial fracturing), well production data, presence of microscale natural fractures, absence of deep cutting faults, formation stress in shale area, and pressure differential between source rock and the reservoir`s bubble point pressure. Efficiency factors for the shale deposits are included in the resource assessment as subcategories – PVT properties, geologic complexity and crystalline structure (EIA, 2013)[1]. There are three main gas factors[1]:

- <u>Favorable gas recovery</u>- 25% of the gas, when low clay, low to moderate complexity and favorable PVT
- <u>Average gas recovery-</u> 20% of the gas, when medium clay, moderate geologic complexity, and overpressure
- <u>Less favorable gas recovery</u>- 15%, when medium to high clay, high complexity, below average PVT

Finally, the geological complexity plays a major role for the accessibility of the shale reservoir formation. Several features can diminish the HC recovery rates: vast fault systems (limiting the extension of horizontal wells); deep seated fault system (vertical faults can cut organically rich shale beddings and introduce water in the shale matrix, reducing the gas filled porosity and capacity of production); and thrust faults or high stress movements (compressional tectonics leads to lateral reservoir stress, reducing the values of permeability of the matrix) (EIA/ARI, 2013)[1].

The three key assessment values derived from the presented step-by-step methodology should be:

- Shale gas in-place concentration – defines the abundance of the shale formation resource, in *Bcf/mi²*
- Risked Shale gas and Shale oil in place – reported in *BCF or TCF* of shale gas
- Risked recoverable gas and oil – in *TCF* of shale gas

A comparison summary table (Table 6) for a typical overview of the assessment results for shale gas in Scandinavia is depicted below (EIA/ARI, 2013)[1].

	Basin/Gross Area		Scandinavia Region (90,000 mi^2)	
Basic Data	Shale Formation		Alum Shale - Sweden	Alum Shale - Denmark
	Geologic Age		Cambro-Ordovician	Cambro-Ordovician
	Depositional Environment		Marine	Marine
Physical Extent	Prospective Area (mi^2)		2,120	5,980
	Thickness (ft)	Organically Rich	250	250
		Net	200	200
	Depth (ft)	Interval	3,300 - 7,000	11,000 - 15,000
		Average	5,000	13,500
Reservoir Properties	Reservoir Pressure		Normal	Normal
	Average TOC (wt. %)		7.5%	7.5%
	Thermal Maturity (% Ro)		2.00%	2.00%
	Clay Content		Low	Low
Resource	Gas Phase		Dry Gas	Dry Gas
	GIP Concentration (Bcf/mi^2)		76.8	110.5
	Risked GIP (Tcf)		48.9	158.6
	Risked Recoverable (Tcf)		9.8	31.7

Table 6 Shale gas reservoir properties and resource in Scandinavia (Alum Shale), showing the 31.7 TCF of technically recoverable resource in the Cambro-Ordovician organically rich shale on the territory of Denmark. (EIA,ARI Annual Outlook, 2013)

6.2. New approach applied for the Danish Alum Shale resources

The idea behind this new method for the investigation of recoverable reserves of shale gas in Denmark will be partly to combine three other evaluation techniques, with a self-sufficient pattern of parameters in the study and coherent adjustment of the data. Three autonomous previous studies from different sources have been used:

- USGS FORSPAN model for assessing technically recoverable reserves in Alum Shale
- EIA/ARI research for shale basins in Europe, 2013
- Alaska North Slope methodology characterization parameters and quality of probability distribution
- Others – GEUS, GASH, independent papers (Schovsbo, 2006, 2013; Gasparik, 2013; Schultz 2013, Pool et al. 2012, etc.)[1]

A combination of estimations from each report, will be compared with the distribution mechanism for the parameters in Alum Shale, and layout sections within an excel file sheet (Appendix A) are prepared for overall implementation of the new approach. The main reason for editing and modifying the other former assessments will be to make an overview, control and conclude whether a median or mean outcome can be reasonable and precise on a different continuous petroleum reserves` basis. The aim of the common agglomerated data from several studies will either prove their certainty or visualize an offset within considerable boundaries. The independent studies include critical reservoir engineering calculations, along with nano-pore throat parameters, sorption indexes, TOC and maturity data, porosity correlations, litho-stratigraphic information for Alum Shale, areal extent and AUs, conditional cells of EUR, Langmuir isotherms, shale mineralogical analysis and more. Summary tables, parameter filtering, own calculations for some variables, and comparison between the models, will provide more rigorous assessment configuration. A chronological sequence will be followed in filtering the parameters using the following order of magnitude for the available Alum Shale studies (*EIA/ARI>>USGS>>GEUS>>GASH>>Alaska North Slope Model>>Own Alum Shale results and methods*). The calculation procedure is deployed in Chapter III.

6.3. Pioneer study for the potential in the Lower Carboniferous strata of Bulgaria

For the estimation of the Carboniferous shales on the territory in Bulgaria (J1-well), shale and coal rock samples were provided from well studies in the country. The samples contain different lithotypes from various depths from the Moesian Platform in the Northern part of Bulgaria. Reported inventory (Appendix C) of the received rock samples has been prepared. The Jurassic (Etropole Formation) and Silurian (Lower) shale reservoirs will be discussed for their hydrocarbon potential, in case to provide a full grasp of the unconventional potential in the country.

Several experiments were conducted in collaboration with Aalborg University (Denmark), Sofia University (Bulgaria), Aarhus University and GEUS (Denmark). Those encompassed nano-pore throat analysis of interconnection patterns by a SEM microscopy, bulk mineralogic constituents and crystalline structure method along with determination of macro-fracture system, meso and micro-pore throats and volume percentage of void space in the pores with petrophysical analysis. Geochemical properties of the received debris were estimated from percentage of TOC by RockEval analysis (pyrolysis) and gas chromatography for quantifying the volatile compounds and their composition in the Carboniferous shale/siltstone reservoir. Apart from those experiments, a simple moisture content experiment was run in the laboratory. Thorough interpretation of the results was made, which became the fundament of the new estimation for the potential of shale oil/gas in the C_1 geological succession of the Bulgarian part of the Moesian platform. Polygons of the borehole profile with estimated net shale thickness, depth map and prospective sweet spots were created for the distribution of Trigorska and Konarska Formations.

6.4. Estimated numbers for GIP in Denmark, and Bulgaria given by the agencies

In the following summary table below (Table 7) will be illustrated results from different assessments for shale gas and shale oil applied from agencies on the territory of Denmark, and Bulgaria. This will be a baseline for comparison after the allocation and implementation of the two case study methods in this report for Denmark and Bulgaria. The Poland case study will only provide a theoretical overview of the status for shale gas and oil exploration and production potential. Even though, Poland situates the largest potential in Europe for shale gas production, the project`s scope is limited to analyzing and summarizing the numbers and results given from the agencies for the two mentioned countries. Full-scale visibility of the summary table (Table 7) is available in Appendix B.

Table 7 Shale gas/oil resource estimations for Denmark, Bulgaria and Poland`s TRR, risked GIP and probability success factors

Country	Shale play or formation	EIA play success factors (%)			EIA risked and TRR of shale gas (Tcf)		EIA risked and TRR of shale oil (Bbbl)		Chevron or Kuuskraa et al. 2011	Medlock, Jaffe & Hartley 2012	BGR - Germany (2012)	USGS mean undiscovered shale gas resources (Tcf)	Calculate mean success ration according to USGS method (%)	USGS mean EUR for shale gas for sweet spots (Tcf)	EIA total TRR and risked shale gas for Europe (Tcf)		EIA total TRR and risked shale oil for Europe (Bbbl)		Unproved wet natural gas resources EIA 2013 (Tcf)	Unproved crude oil resources EIA 2013 (Bbbl)
		Play success factor	Prospective area success factor	Composite success factor	Risked shale gas	Technically recoverable reserves (TRR)	Risked shale oil	Technically recoverable reserves (TRR)	Ultimate technically recoverable (Tcf)	Techically recoverable reserves TRR (Tcf)	TRR resources (Tcf)				Risked shale gas	Technically recoverable reserves (TRR)	Risked shale oil	Technically recoverable reserves (TRR)		
Denmark	Alum Shale	60	40	24	159	32	0	0	23	23,5		6.9	40	0.000492					32	0
Bulgaria	Lower Silurian	55	40	22	48	10	2	0,1		-	-	-	-	-						
	L. Jurassic (Etropole)	50	35	18	148	37	8	0,4	8,1	-	-	-	-	-					17	200
	Total (including other)				66	17	10	0,5		-	-	-	-	-						
															4,895	883	1,551	88,6		
Poland	Warsaw trough	100	40	40	532	105	25	1,2												
	Lublin Basin	60	35	21	46	9	0	0	42											
	Podlasie	60	40	24	54	10	12	0,6		120,7	181,5	1.39	45	0.000245					148	3.300
	Kaliningrad/Lithuania	80	40	32	24	2	29	1,4	17											
	Fore Sudetic	50	35	18	107	21	0	0				-								
	Total (including other)				763	148	65	3,3				-								

*Tcf – Trillion Cubic Feet of Gas (1TCF=1000BCF); Bcf = Billion Cubic Feet of Gas; Bbbl – Billion barrels of oil (1bbl = 158.98 liters)

There are two stratigraphic intervals that are prospective for shale gas and shale oil production <u>in Bulgaria</u> – the L.Silurian and L.Jurassic (Etropole), which have been deposited in a marine environment during those geologic times. Both of them are evaluated to have 8 TCF (Chevron) or 10 TCF (BG`s Energy Ministry) recoverable reserves or 37 TCF or risked GIP only for the Middle-Jurassic shale beds (Table 7). Bulgarian assessments of shale gas/oil potential show a minimal data availability from researches, which makes uncertain the baseline positioning of the calculated in-place resources. A third prospective interval, that this thesis will provide, will be the Carboniferous unconventional reservoirs in the Northern territory of the country, and whether they have or not a potential for shale gas/oil production.

On the territory of Poland, due to heterogenic shale formations and the occurrence of different source rocks in different stratigraphic levels, which are geographically scattered, division on five AUs or shale basins is allocated, with some of them including areas from other countries like Ukraine and Lithuania. The five basins are: (i) Baltic Basin – Warsaw trough; (ii) Lublin basin; (iii) Podlasie basin; (iv) Fore Sudetic (Carboniferous); and (v) Baltic-2, Kaliningrad and Lithuania (Table 7). All the basins except number the Fore Sudetic one are formations in the Llandovery group of the Silurian period. Numbers for GIP fluctuate drastically, with most realistic value for TRR of 1.4 TCF (USGS, 2012) (Table 7).

The offset in the numbers of the assessments between USGS and EIA for the Danish Alum Shale formation, seems to be with the same trend, due to the huge uncertainties in the shale gas play. In Poland`s numbers, distinctive entities of shale gas areas, and exploration wells have been delineated, that approved and consolidated the geological information for interpretation, whilst in Denmark the exploration stage has fairly begun. USGS points out the mean number of 7 TCF of undiscovered shale gas in the Alum Shale (Table 7), while the EIA/ARI report[1], sets a risked recoverable shale gas resources in the Alum Shale of 32 TCF (Table 7). An arguable critique for the mismatching of the numbers is the baseline methodology, which is crucial in any case for calculating resources. The FORSPAN method that USGS uses has different step-by-step procedures in the assessment, whereas the EIA/ARI methodology for GIP follows a contrast procedure.

7. Goals, delimitation and focus of the project research

After revising the technical literature and familiarizing with the characteristics of the continuous petroleum accumulations, in particular shale gas and shale oil properties, the main tasks expected to be achieved in the scope of the thesis were decided. A solution strategy is illustrated in the diagram below where the workflow can be monitored, along with the goals needed to be achieved:

- The overall goal with this pilot study is to acquire an independent, scientific based, evaluation assessment of the resources in the Baltic Basin and Moesian Platform by combining the knowledge from each survey into a basin wide synthesis, which will result in product improvement and less deviation from realistic resource in-place;
- Evaluating the shale gas/oil resources for the Alum Shale formation, with a combination of parameters derived from several estimations, and accounted for different screening criteria that could have an impact on the in-place resource, which led to reduce prospective area;
- By following the ARI methodology 2013 from their report[1], and the sweet spot delineation with EUR values from the USGS assessment for the Danish Alum Shale, new interactive map of the sweet spots was made;
- Establishing a pioneer shale gas assessment for the territory of Bulgaria, with emphasize on a third shale interval – Carboniferous (Konarska and Trigorska Formations);
- Interpretation of rock samples BG1.1-J1, BG1-J1, BG2-J1, and BG3-J1 (Appendix C) and introducing the results for the evaluation of the assessment area, geological parameters of the reservoir, maturity level and drawing polygons for prospective core area of the play.

Conclusion

Due to the high complexity of the shale gas/oil resources, the methods for their evaluation are not still well developed and with the needed accuracy. The deviation from a mean value for the shale resources and reserves, taking into account the large number of agencies and companies involved in the assessment stage, advocates the uncertainty of such numerical prognosis. Differences in the magnitude of tens to hundreds of Bcf of gas, for the shale resources in-place, constitutes for wide range in the numbers of the variables used, and the procedures for the engineering calculation approach.

Figure 32 Thesis`s disposition plan, and preliminary task designation

CHAPTER III – Shale gas potential in some European countries: Case study section – Denmark and Bulgaria

8. Calculations for resource assessment of shale gas in Denmark

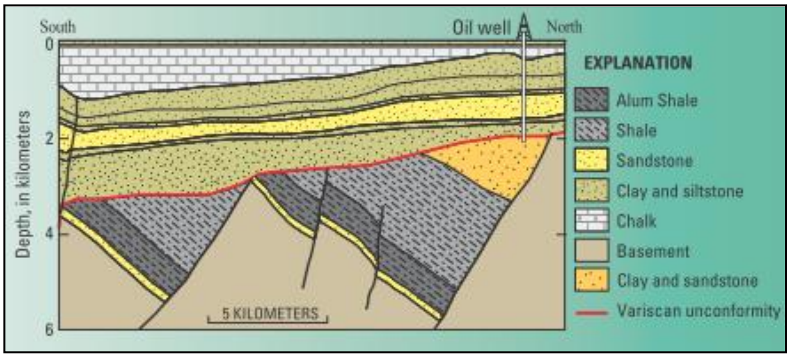
Shale gas exploration in Denmark is in its earliest phase, which in part is reflected in the wide range of resource estimates for the play. The need of data from new wells drilled in the core area (sweet spots) that will commence in 2014-2015, will shed new light on the geology and provide more rigorous data for future assessments. The testing of the shales in Julland and Sjælland may provide better results for the company than the boreholes of Southern Sweden did for Shell (Pool et al., 2012).

8.1 Geological background

Organic-rich fine grained sedimentary rocks of Middle Cambrian to Early Ordovician age, lower to mid Jurassic are present onshore Denmark. The black shales of the Lower Paleozoic holds the main potential for shale gas extraction, whereas the Mesozoic shales are thermally immature in the deepest parts of the Norwegian-Danish Basin (Petersen et al. 2008, Schovsbo et al, 2011, in press, Gautier et al., 2013). From the Paleozoic strata, the Cambrian to Lower Ordovician Alum Shale is the thickest and richest, and the major assessment unit on the territory of Denmark (Gautier et al., 2013).

8.1.1. Paleogeological setup of Alum Shale

The depositional environment, paleo-geography and structural and tectonic movements (faults, erosion, subsidence) are the main controlling factors for the widely distributed reservoirs to retain their gaseous or liquid phase during the evolution of the deposit. In great importance for Alum Shale is the geology, where the main events in Baltica during the Early Paleozoic played a major role for the evolution of the shale reservoir. Before the Caledonian front, closure of the seas took place in Late Ordovician and Silurian, with an accompanied subduction phase., which position is unknown exactly (Sturt & Ramsay 1999), but it is certain that the subduction was on two fronts, including one between Baltica and Laurentia and another between Baltica and Avalonia (Torsvik et al., 1996). The burial and generation of gas in the Alum Shale probably started in the Late Silurian in a Caledonian foreland basin (Gautier et al., 2013).



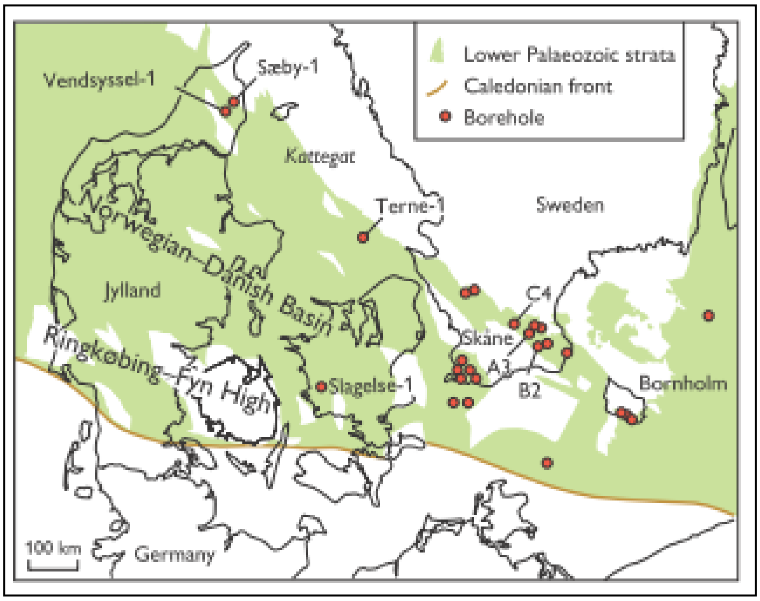
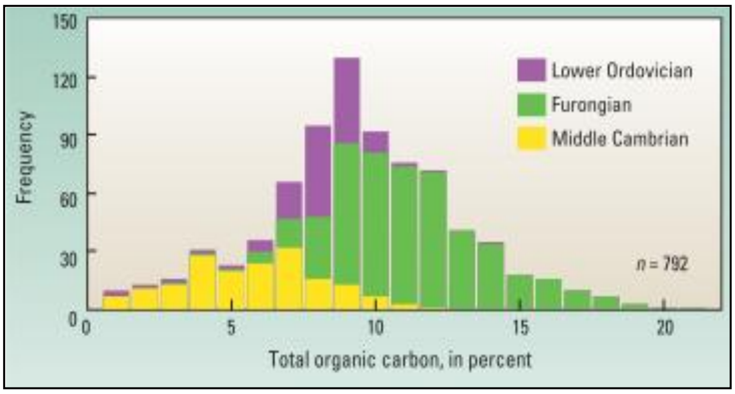


Figure 33 Cross section of stratigraphy in northern Julland depicting the Paleozoic Alum Shale positioned in tilted fault blocks (vertical exaggeration x2) (Gautier et al., 2013) (left) and simplified distribution of Lower Paleozoic strata in Denmark with borehole location for geological assessment of Alum Shale (Schovsbo et al., in press) (right).

Oil and subsequently gas was produced in the Silurian, and in the Carboniferous and Permian times, the shale exerted structural deformation which resulted in faults, tilting and erosion of the deposit (Ramsay, 1999). The blocks, in which the Alum Shale is preserved, are beneath the Variscan unconformity and are overlain with Zechstein (Figure 33) strata. During Mesozoic several subsidence stages controlled the reburial of Alum Shale, and in the Late Neogene uplift occurred along with the following Pleistocene erosion. The main intensive thermal rank exerted in the Paleozoic did not occurred in the reburial stage later in the Mesozoic and Palaeogenic times, in the Terne-1 area (Gautier et al., 2013), but it is not excluded that some shale formations might have retained hydrocarbons, or generated additional quantities during Mesozoic times (Gautier et al., 2013). The Cambro-Ordovician shale is located in the northern part of Europe, and is mainly considered thermally mature and overmature in the southern area of the formation (Denmark and Sweden), and immature in central Sweden (Pool et al., 2012).

Alum Shale contains two types of illite – reflecting detrial and illite from the weathering of smectite derived from volcanic ash in Permian and Carboniferous times (Lindgreen et al., 2000). The low-energy paleo environment of deposition for the marine Alum Shale, the anoxic conditions (Pedersen, 1989), the intrebedding mudstone-shale facies and the TOC quantity of up to 25% (Nielsen and Schovsbo, 2006), ranks the shale formation as a prospective shale gas target in Denmark. Porosity in Alum includes intergranular and intragranular pores, related with clay and OM, phyllosilicate compounds (Gasparik, 2012). In addition the shale comprises of three members, which are different in distribution, texture and composition – Lower member (Middle Cambrian); Middle member (Furongian), Cambrian; and Upper member (Early Ordovician) (Figure 34 left).



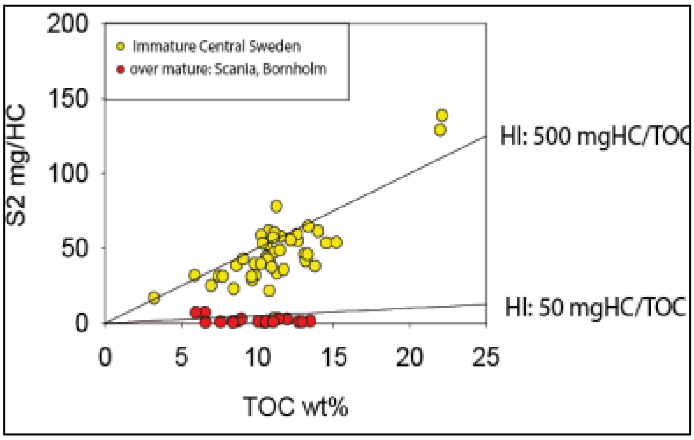


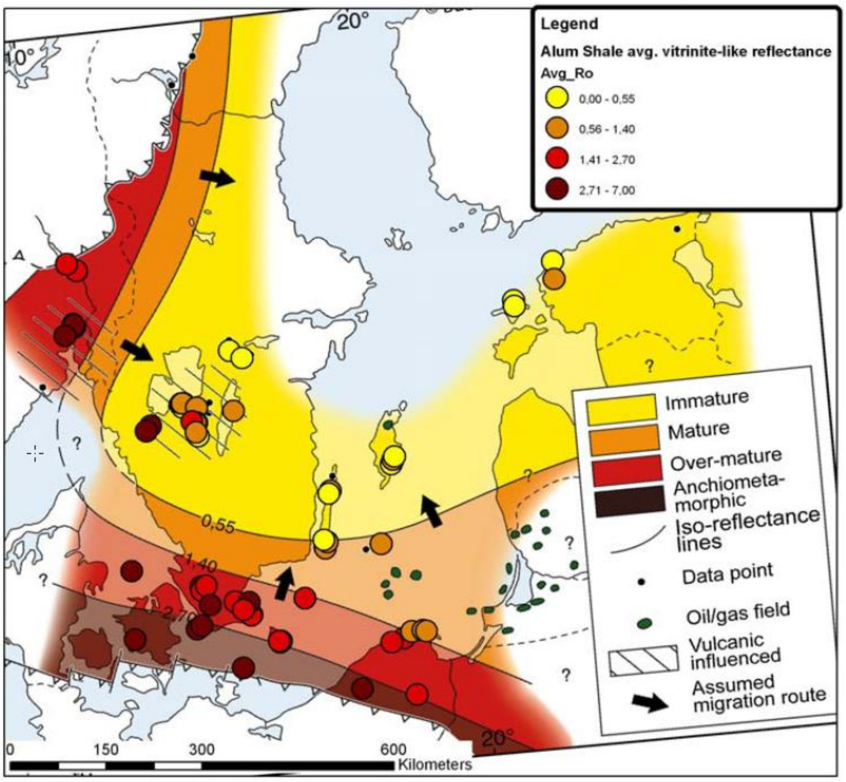
Figure 34 Distribution of TOC in different members of Alum Shale (Schovsbo et al., 2011) (left) and quantity of total organic carbon (TOC) in Central Sweden and Scania, Bornholm

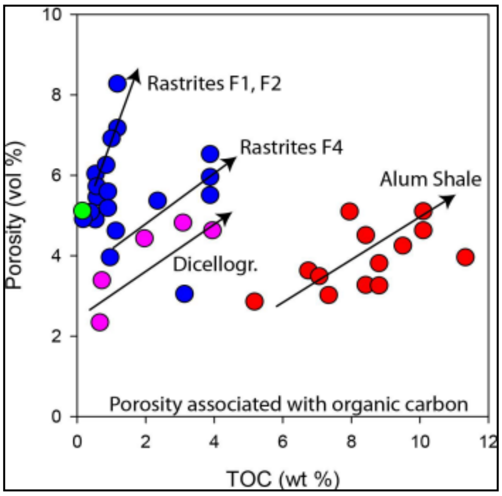
The Furongian member is the thickest one in northern Denmark, with anoxic deposition (Schovsbo, 2001), and is considered the major productive shale reservoir for gas potential in Denmark. TOC varies with stratigraphy, where the Middle Cambrian Alum has least TOC, Upper Cambrian (Furongian) Alum Shale has the highest TOC, and the Lower Ordovician Alum intermediately organic-rich (Figure 34 right).

8.1.2. Reservoir Parameters of Alum Shale

Wells drilled on Bornholm aimed mainly to obtain new data comprising of core samples, stratigraphic and geochemical information (Schovsbo et al., 2011) (Figure 33 right). Thickness of Alum Shale (Buchardt et al. 1997) is 180 m offshore (Terne-1 well) and 30-100 m onshore.

The first shale gas exploration well aiming at the Paleozoic strata in Denmark - Vendsyssel-1, will be drilled in Julland in 2015 by Total E&P (Schovsbo et al, in press)[1]. The research before, was mainly done by GEUS, which evaluated the onshore shale gas prospective, based on coring data from the island of Bornholm, where the Alum Shale strata is shallow buried and beneath a Quaternary seal (Schovsbo et al. 2011). Alum Shale`s TOC ranges from 4 to 18 %, with mean values 6-10% (Appendix A). A variation for TOC between 0 and 15 % is assumed for the Alum Shale composite parameters table in this report (Appendix A). A certain trend for loss of organic matter with maturity can be concluded when comparing the different ranks of thermal evolution – immature with TOC 8-12% and mature (dry gas) with 6 to 8% TOC. Generated oils have been trapped in the matrix and cracks during later stage of maturation, which caused a temporary plateau stage in TOC decrease. The borehole drilled in Kattegat in 1985, revealed the gross interval mentioned (180 m) (Schovsbo et al. 2013). Alum Shale has abundance of organic matter, characterized by kerogen type II, with a marine deposition, which yields not the typical petroleum derivates, but light hydrocarbons (such as condensate, wet gas, light oil).In addition, the unlikely OM in the shale (described as kerogen type I (Pedersen, 1989) and type II by (Bharati et al. 1995), arrived from algal material that generated gaseous pyrolysis products with aromatic oils upon heating. This infers for high gas/oil ratio in the shale reservoir. The unlikely specifications of the kerogen might also affected from irradiation damage (uranium concentration in Alum is 100-300 ppm, Schovsbo, 2002) or from unusual OM source. On the other hand, organic carbon in Alum is controlled by Late Silurian and Early Devonian burial of the shale, which caused maturation in the ankimetamorphic facies and further expulsion of some organic components, which lowered the carbon content with up to 50% (Buchardt et al. 1986). The shale gas potential of the Alum Shale results from: the high thermal maturity indexes of the vitrinite reflectance values, and the deep burial along with high geothermal gradient in the Late Silurian-Early Devonian time (Buchardt et al. 1997). The vitrinite like-particles were converted to graptolite reflectance equivalent of vitrinite (detailed trilobite and graptolite zonation, with complete shale section in Bornholm, because of specific maturation of the Alum Shale vitrinite at lower temperatures (Petersen et al. 2013). The Lower Paleozoic (Caledonian) burial led to thermal maturity for oil and gas (more than 2% graptolite reflectance, which is the equivalent of 1.6% Ro) for most of Alum Shale`s area (Buchardt et al. 1997; Petersen et al. 2013), where as Alum in the shallow research well of Skelbro-2 had VR_o of 2.4%, which infers for overmature state of the shale (Figure 35 left).





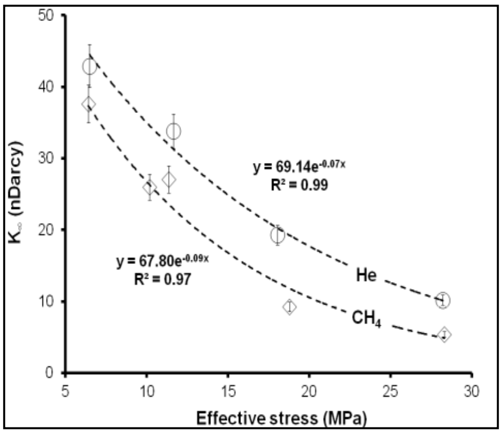
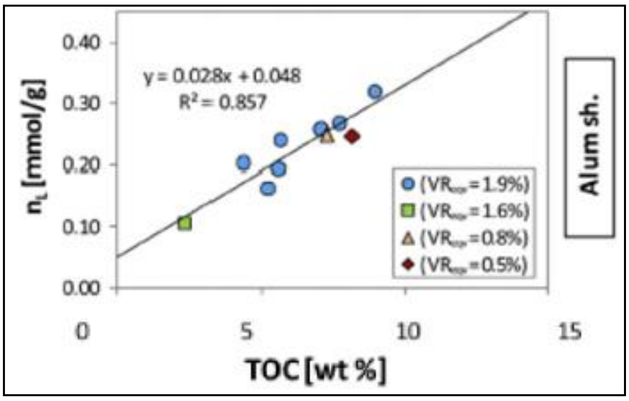


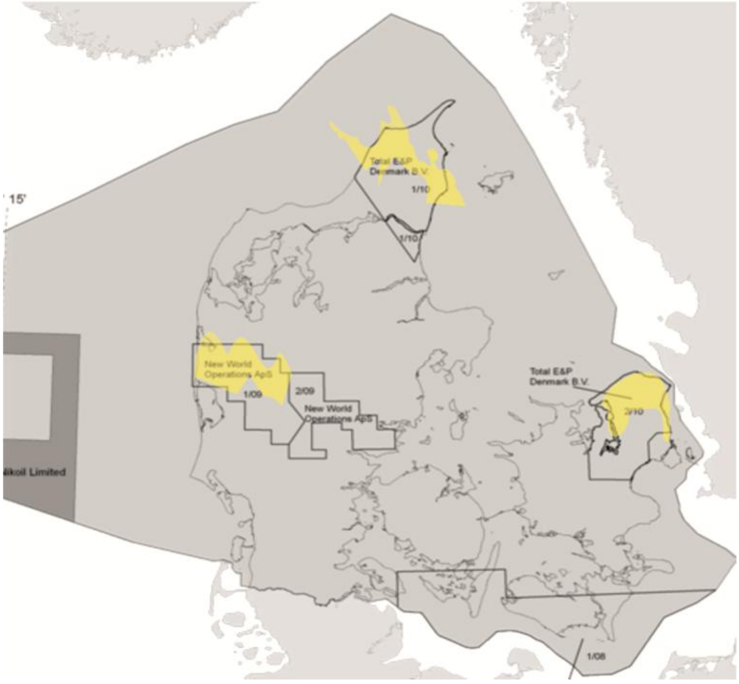
Figure 35 Maturity of Lower Paleozoic sequence based on reflectance of vitrinite-like particles (maturity increases towards Caledonian front, reflecting deep burial in Late Silurian and Early Devonian) (left) and three relationships of Alum Shale parameters – Porosity and TOC (up-right), Permeability (k) and Effective stress (center-right) and Langmuir volume (n_L) with TOC (down-right) (Petersen et al.2012, Gasparik, 2013, Ghanizadeh, 2013)

Other definitive reservoir parameters of the Cambro-Ordovician shale are a matrix permeability of 40 nDarcy (Figure 35 center-right), low adsorption volume capacity (n_L) and mean porosity values of 8-12% (Figure 35 center-right). Gas saturation (Sg) in Scania (Southern Sweden) was concluded to be as high as 20% (Pool et al. 2012). Alum contains both adsorbed and free gas, where linear relationship between porosity and TOC exists, governed by geochemical properties (maturation) (Figure 35).



8.1.3 Prospective area delineation of Alum Shale for the assessment

The continuous type gas resources in the Paleozoic of Denmark (Alum Shale) had lately drawn interest towards production of shale gas from the French company of Total E&P, due to prospective future exploration in Northern Denmark and already established research wells on the island of Bornholm. Nevertheless, the scarce geological data, uncertainties for some reservoir properties of the shale, and wide range of estimates existing for shale gas/oil resources in the delineated area, the new evaluations by USGS from 2013 with total mean gas quantity of 6.95 TCF, are quite promising (Gautier et al. 2013)[1]. This number equals to the consumption rate of natural gas in Denmark for the next 35 years to come (gas consumption in Denmark for 2012 accounts for190 BCF/per year) (DEA, 2012).



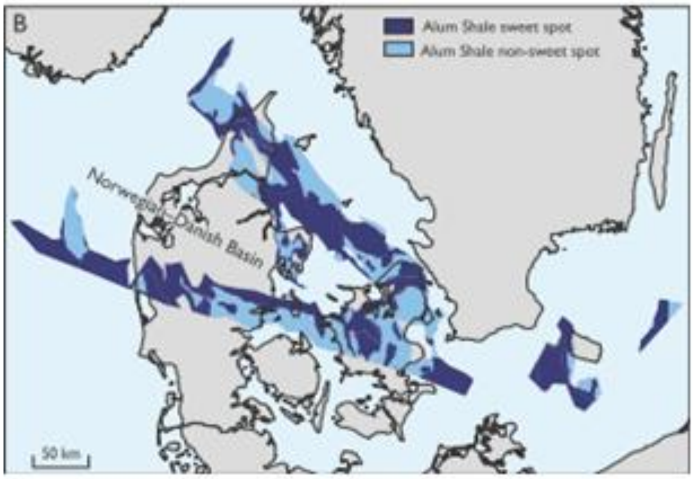


Figure 36 Shale gas exploration windows given to Total E&P on the license procedure with overlapped sweet spots from the GIS model adopted from Lassen & Tybo (2012) (left) (after NAG, 2013) and prospective area for shale gas exploration on the territory of Denmark (Schovsbo et al, in press) (right)

In Denmark two shale gas exploration licenses awarded under the Danish "Open Door Procedure", both licenses are currently held by Total E&P Denmark B.V. (Figure 36 left). Prospective area maps were used for the creation of the criterion for higher than 20 m thickness of Alum Shale and burial depth between 1.5 and 7 km (Gautier et al., 2013). Deeper areas of the shale are not feasible for exploration (central part of the Norwegian-Danish Basin).

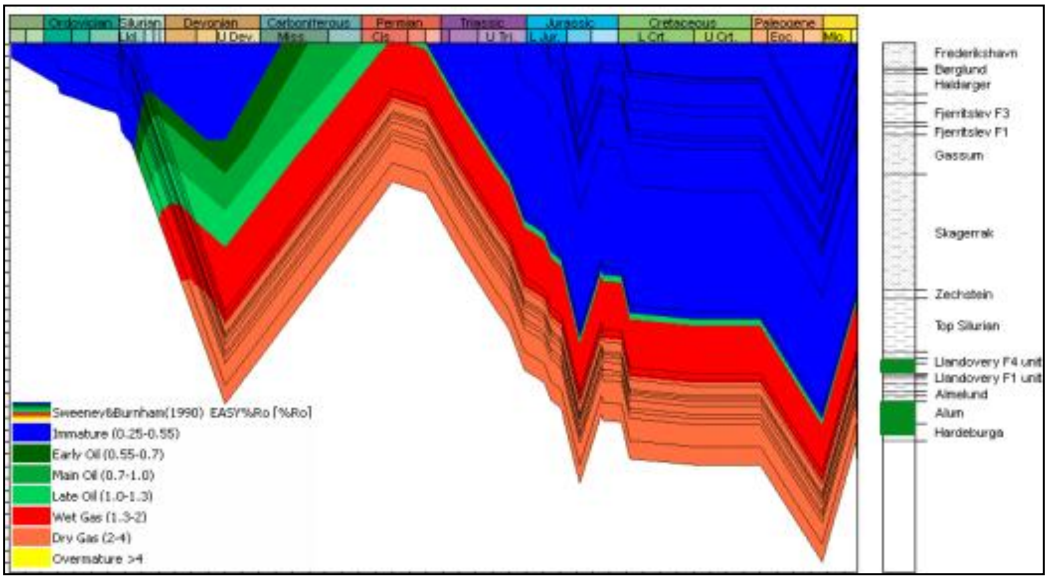
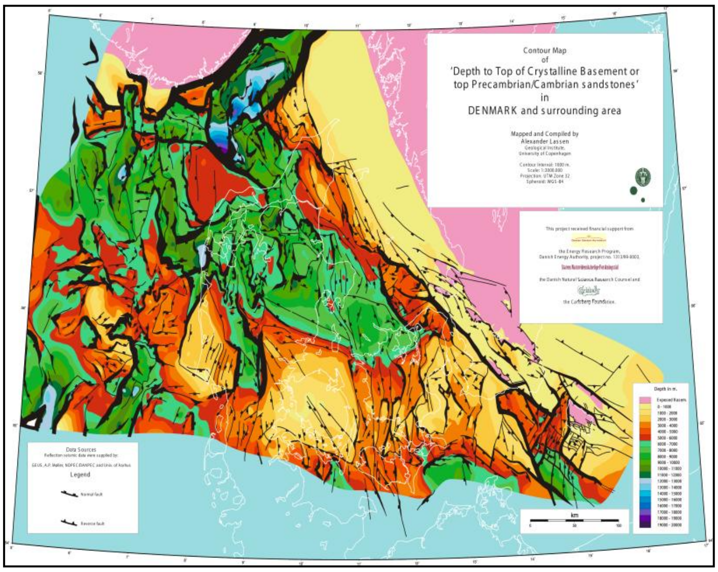


Figure 37 Simulation of hydrocarbon generation and burial history of Kattegat area (Terne-1 well) (Don Gautier, 2013).

The potential of Alum Shale on the territory of South Sweden was concluded to be low, because of shallow depths (700 m) and lack of economical quantities of gas for potentially productive play (Pool et al. 2012). Perhaps the gas loss, was due to faulting, fracturing, pressure reduction during uplift, and paleo-erosion conditions occurred in the Early Devonian in Skåne`s area of the Alum Shale (Pool et al., 2012). Conversely, in Denmark the Cambro-Ordovician shale was reburied in the Cretaceous and Palaeogen periods, which led to gas retention and kept the reservoir integrity. Still, there are supposedly some areas with high risk of gas leakage in the Paleozoic of Denmark (Gautier et al., 2013).

Differently preserved thickness of the Alum Shale, is another reason for diminishing the assessment area. Depressurized areas have high risk for retaining the volatile HC phase. Thus a lower threshold of 1.5 km of overlaid strata on Alum Shale is a marginal assumption for full-integrity of the reservoir (Figure 36 right). The potential localities of the shale prospects are situated in fault-block systems of the Paleozoic strata in Denmark, which are overlaid with more than a kilometer deep Paleozoic deposits (Figure 38 left) (Schovsbo et al. 2013). The areas where such sedimentation over the shale is absent, are deemed to be non-prospective and non-sweet spot (Gautier et al. 2013)[1]. Furthermore, time as a control factor during maturation and uplift poses risk for reservoir erosion and gas retention of Alum Shale in Denmark. Because of no actual data for gas saturation and HC presence, the recent USGS assessmnent[1] included an adjustment of the EUR and success ratios to the different areas (sweet spots and non-sweet spots), by adaption, so that the gas content retained from the different uplift events could be matched carefully (Gautier et al. 2013). Division of the prospective area in the whole TPS (i.e. Alum Shale basin) is on two autonomous units (AUs) – offshore and onshore.



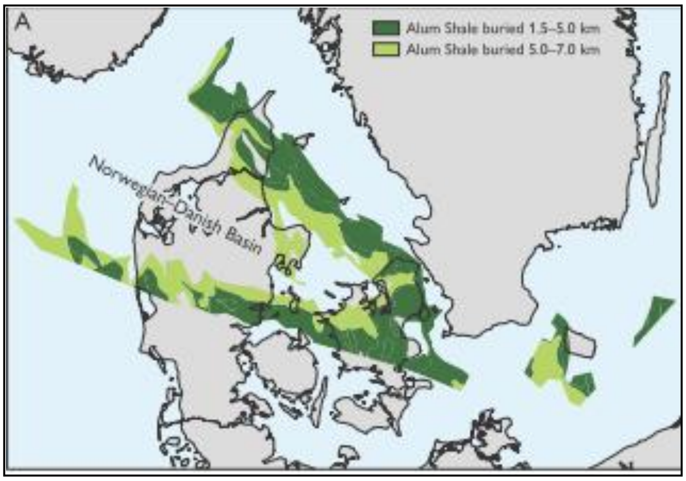


Figure 38 Depth of Pz basement (Lassen & Thybo, 2012) (left), and burial depth delineation area for Alum Shale (right), where the two areas (1.5-5 km and 5-7 km) are build in a geological mode based on the depth distribution range of Alum (left) and a correction for the thickness of the Pz strata by that specifying the risked depressurized spots in the shale (Schovsbo et al., in press).

The main cells in the area with sweet spots` properties, are situated in the fault blocks that hold the Furongian Alum Shale and where thick post-Alum Paleozoic strata is encountered (Figure 38 left) (Gautier et al. 2013). Those places coincide with less intense erosion and surface exhumation of the shale to the late Paleozoic uplift and high probability of gas retention. The TRR in both AUs estimated by USGS report[1], hold the mean value of 6.9 TCF (Gautier et al. 2013). Conversely, a quadrupled number of recoverable resources has derived from the EIA assessment with the agency`s 23 TCF evaluation potential in 2011, and the even higher 31 TCF in 2013 (ARI, 2013)[1].

8.2. Calculations for risked GIP and TRR

The assessment methodology that this report will incorporate, will take the advantages of the two evaluations executed for the Danish Alum. The full screening criteria and parameters for the Cambro-Ordovician shale can be tracked in Appendix A, where 24 different reservoir and geological parameters are combined from 12 different sources that have investigated the Alum Shale. Several modifications for the evaluation procedure given from EIA in its Annual Energy Outlook from 2013[1] (described in Chapter II) were applied, including different volumetric method approach and more accurate values for adsorbed gas calculations (Langmuir volume and Langmuir pressure). On the other hand the delineation area of the total petroleum system (TPS) and the assessment units (AUs) calculated in the USGS/GEUS shale gas and oil resource potential of Alum Shale (Gautier et al. 2013) were significantly changed with integrated theoretical model of different gas states (free and adsorbed) distribution, derived by accounting for burial depth and EUR data. This was done in order to develop a projection which more realistically defines technically and economically recoverable reserves in Denmark, even though the outcome achieved from USGS (6.9 TCF) looks quite reasonable.

Because of no production yet of shale gas in Denmark, actual data for fluid behavior, reservoir PVT patterns, adsorbed and free gas ratio, and actual pressure drop data during gas extraction is not available. This is why an additional calculation for cumulative gas for future production is added to the typical volumetric data and in-place resource estimation procedure, so that it can depict a theoretical recoverable ratio. This will approve the certainty of the calculations, in long-term manner and account for time-related production, with decrease in reservoir (formation) pressure during extraction. Simulating the in-place resource at different pressures after completion stage ends and production of fluids starts, contributes to better preceded visualization of decline rates and resource extraction rate.

The recovery factor index is complexly controlled and determine by the assessor on the basis of combined pre-assessment data and parameters, such as clay content, structural complexity of the formation, and economical reserves in-place (is hydraulic-fracturing applicable or not).

At present, there is a vast onshore area interpreted by the USGS report[1], inferring for 13000 km^2 onshore and 19000 km^2 offshore. The de-risked area for Alum Shale for the polygons is based on minimum depth of 1.5 km, thickness interpretation of Alum in different areas of more than 20 m, selection of three AUs (onshore (shallow 1.5-5 km), onshore (deep 5-7 km) and offshore – 1.5 to 7), bounded by the S margin of Baltica due to uplift and erosion, and bottom line of vitrinite reflectance of 4% at present distribution to the cut-off depth of 7 km (Schovsbo 2013).

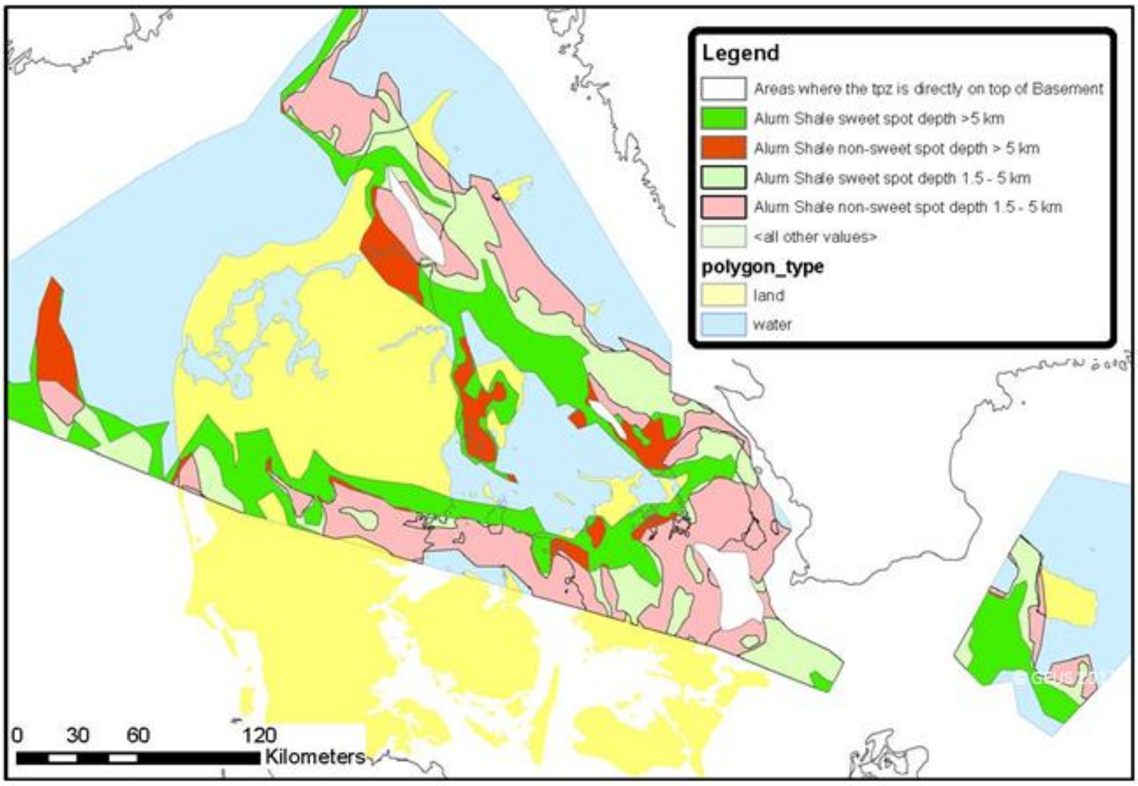


Figure 39 Potential localities for shale gas in Denmark with depiction of high probability points of deep buried Alum Shale exploitation (NAG Directors PP, 2013)

8.2.1. Procedure and approach for calculating the shale gas resources in Alum Shale

Triangular distribution is used in the assessment, due to the sharp proportions of the low and high-ends configuring the mean value. Furthermore, this pattern may not show high values of the area or the Risked GIP. The fluctuations of numbers require skewing, and thus three values were needed in the description of both Risked GIP and TRR: Minimum, Maximum and a central fixed value (Mean) (Figure 40).

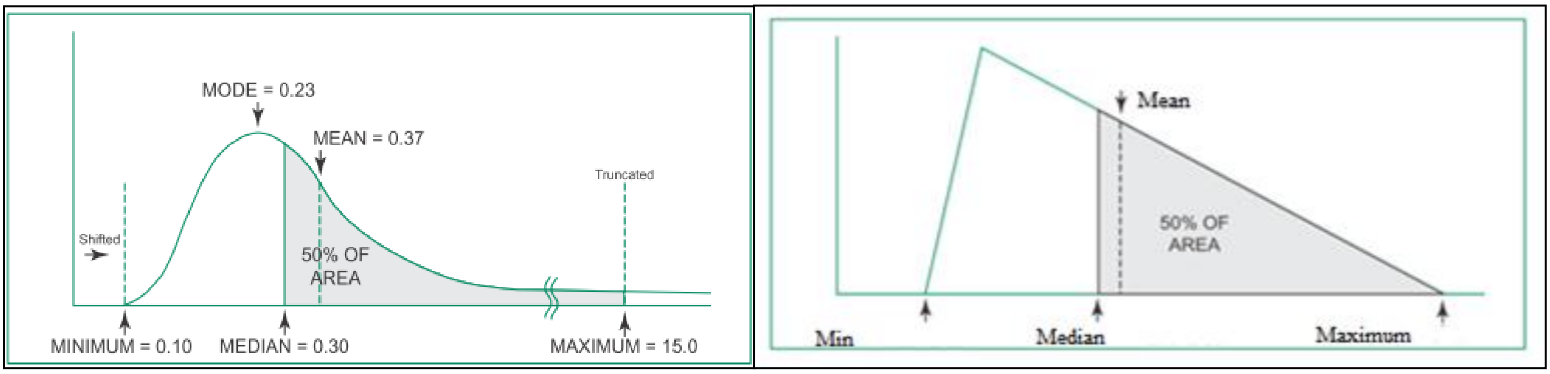


Figure 40 Components of one skewed triangular distribution probability for TRR (right) and lognormal distribution (left) (Modified after USGS, 2012, FORSPAN Paper)

All the minimum, maximum and mean values for the parameters of Alum Shale are shown in the composite table in Appendix A. The Optimal GIP (GIP_{opt}) calculation should be recognized as the true and realistic resource, because of the median and moderate values of probability taken in this report for the Alum Shale reservoir parameters.

The total area containing the future prospects of shale gas extraction in the delineation of Alum Shale should consider reduction, because of the following assumptions and considerations:

- High-level of heterogenicy in lateral and vertical direction of Alum Shale;
- Insufficient volumetric data for the reservoir in some localities;
- Dominance of sorbed gaseous state with hard expulsion conditions;
- High geological complexity - detrial tilted fault structure of deposition;
- High water content – in the vicinity of 80% discovered in some parts of Alum Shale – S_g less than 30%, gas flow rates maybe small in some parts of the prospective area (minimized gas capacity)
- Multi-component gas mixtures-heavier hydrocarbons exist in natural gas (ethane, propane), which may lead to some liquid (condensate) fluids to be recovered. They have different behavior (non-ideal), which will change the FVF (B_g) and volume data in respect to compressibility. Binary system, mixed rules should be applied, and accounted for non-organic gases such as CO_2, which can show competitive storage to methane sorption.
- Change of porosity and sorption capacity under different effective stress conditions would have to be reconsidered, because shales below 5000 m are deemed non-prospective because of extremely low permeability values and high production costs. All the points mentioned leave 20% for the mean portion of the sweet spots in the total area of Alum Shale (Figure 41)

The probability values for the optimal (GIP_{opt}) assessment potential assume 15% less prospective area onshore and a bigger degree of reduction offshore (25%), due to the incorporated arguments, which concludes for 10500 km^2 (2600000 acres) (Table 8). With this consideration and the range of the area for the mean, minimum and maximum projections, depicted in Appendix A, the proportions for the new area considered are as tabulated below.

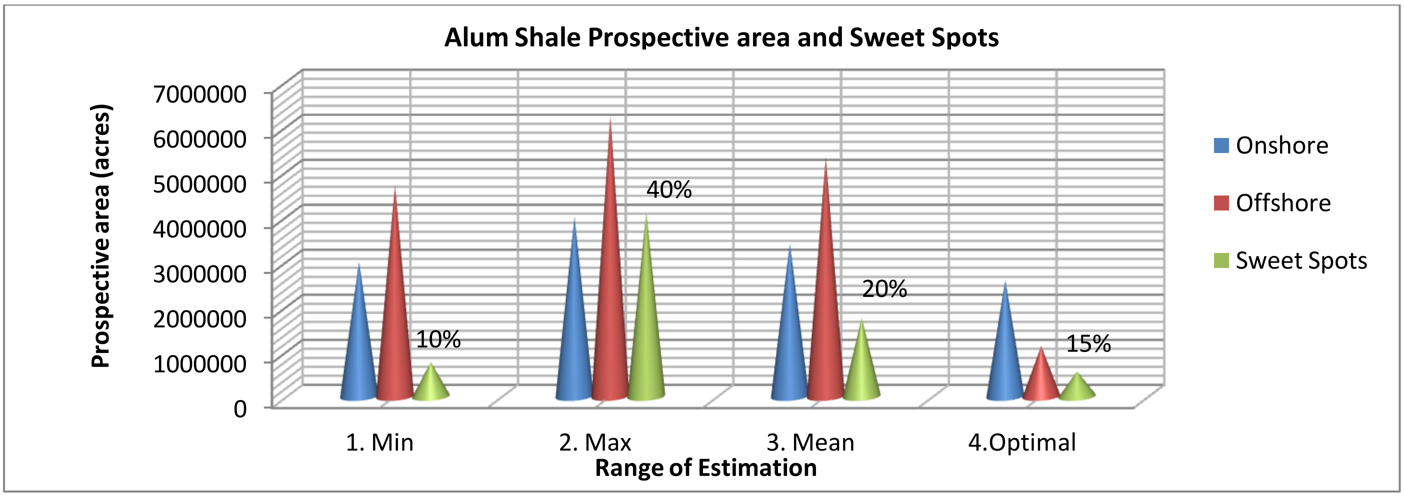


Figure 41 Proportions in percentage of sweet-spot areas in Alum Shale and size of prospective area (in acres) considered in this study

This new division of the spatial extent of Alum Shale derives different proportions in the depth range between 1 and 5 km, with mean values (green) of 2000000 acres (3125 mi^2). The delineated parts for the new area in this study for the different depth ranges (Figure 42) are calculated by the ratio form the GIS model represented up (Figure 39), but for the smaller size of the area assumed.

High expectations area situated in the optimal depth range (1-5 km) is about 30% of the total delineated projection, from which probably only 50% will be explored in the future development of shale gas in Denmark. The other part is (1st and 2nd pillars in Figure 42) mainly a non-sweet spot area with low overburden strata, depressurized (uplift in Upper Paleozoic may to risks of gas retention) or unfavorable reservoir conditions and screening parameters (thickness, thermal maturity, TOC, gas saturation and water occupying the pore space). Furthermore, some of the offshore area will not encounter any shale gas development soon, due to lack of any production in the world yet from offshore shale gas boreholes.

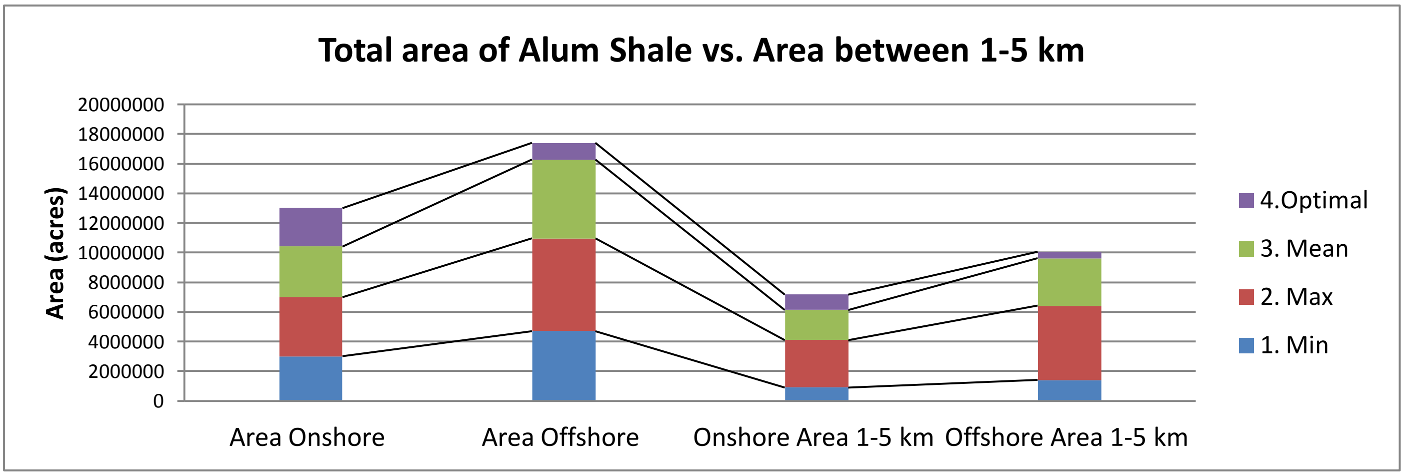


Figure 42 Prospective area distribution in the offshore and onshore AU and in the depth interval between 1 and 5 km

The calculation procedure overtaken in the report is as follows:

Step 1: Estimation of free gas in-place resources (GIP) by the volumetric method

Gas in place by the volumetric method is given:

$$GIP = \frac{V_b(p)(1-S_w)}{B_g(p)} \qquad (20)$$

- GIP – Gas in place
- V_b – 43,560 x A x h x ϕ = bulk reservoir volume, ft^3
- 43,560 - ft^3 per acre-foot
- A – Area, acres
- h – Thickness, ft
- ϕ (p) – porosity at reservoir pressure (p), fraction
- S_w – water saturation, fraction
- $(1-S_w)$ – Gas saturation (S_g), fraction
- B_G – Gas formation volume factor at reservoir pressure p, ft^3/SCF
- p – Reservoir pressure, psia

The method suits the territory of Denmark for potential shale gas estimation, because it is used before any production is established, and by that determines the range of the GIP per acre-foot of bulk reservoir rock.

Input parameters for the equation (20) above are tabulated in Table 8, where a constant gross thickness with a mean value of 311 ft has been assigned with high Net to Gross ratio (N/G) in the shale (up to 80%). Thus almost the full thickness of the shale is assumed as organically-rich (initial range is 200 to 350 ft) (Appendix A).

Table 8 Critical reservoir parameters for Alum Shale estimation of resources in-place

Range	Area Onshore (acres)	Area Offshore (acres)	Net Thickness (ft)	ρ (g/cm3)	Φ(%)	P (psi)	T (F)	Z	Bg	Sg (%)	V_L mmol/g TOC	P_L mmol/g TOC
1. Min	2999859	4700000	164.5	2.3	4	2945	147	0.93	0.0053	15	0.8	2.62
2. Max	3999894	6250000	656.7	2.6	12	11704	395	1.53	0.0031	80	4.2	10
3. Mean	3408324	5330667	311.1	2.5	7	7106	275	1.17	0.0034	50	2.5	6,25
4.Optimal	2594606	1120000	426.5	2.45	7	8702	329	0.894	0.0033	20	0.28	4.16

Estimation procedure for the onshore AU resources of shale gas in Denmark will be present, whilst the results for the offshore AU will be calculated by the same method and will be tabulated. The following methodology uses corrections for the Langmuir Volume, which are applied for the mean and optimal values.

Calculation of minimum, maximum, mean and optimal gross reservoir volume (V_b):

$$\boldsymbol{V_b = 43,560.A.h.\phi}$$

$$V_B^{min} = 43560.(2999859).164.0.04 = \mathbf{857}\ billion\ cubic\ feet\ (\boldsymbol{Bcf})$$

$$V_B^{max} = 43560.(3999894).656.0.12 = \mathbf{13}\ trillion\ cubic\ feet\ (\boldsymbol{Tcf})$$

$$V_B^{mean} = 43560.(3408324).311.0.07 = \mathbf{3}\ \boldsymbol{Tcf}$$

$$V_B^{opt} = 43560.(2594606).426.0.07 = \mathbf{3}\ \boldsymbol{Tcf}$$

Step 1.2: Calculation the formation volume factor (Bg) and compressibility factor for different pressures and temperatures

In such calculations, it should always be accounted for the gas generation and pressurization in shale rocks (source and reservoir) by setting the resistance force (capillary pressure) and natural gas gravity in the different laminas in the shale gas reservoir, along with the driving forces of migration (pressure of free natural gas) in the laminated beds. By comparing the both forces it can be concluded if either migration can occur (driving force >> resistance force), or cannot in different laminated layers (resistance force > driving force) is shale. The pressurization is dependent on the volume formation factor given as:

$$p_{gas} = f(B_g)\ and\ B_g = \frac{v_p - v_w - v_o}{v_g} = \frac{(1 - s_w - s_o)h_s.\phi.10^6}{Q_{gas} - Q_{miss} - Q_{exp}} \tag{21}$$

Where p_{gas} (atm) is the pressure generated by gas expulsion in shale; B_g is the volume coefficient (m^3/m^3); V_p is the pore volume of shale; V_w (m^3) is the pore water volume of shale; V_o (m^3) is the oil volume (if any); V_g is the volume of free gas in shale; Q_{gas} is the generated volume of gas in shale; Q_{miss} is adsorbed, dissolved and diffused natural gas in shale; and Q_{exp} is the volume of expelled free gas generated by an elemental area of shale (initial value is 0), all Q given in m^3/km^2.

The FVF is specified and will be used in the calculation procedure in the following form:

$$B_g = \frac{P_{sc}}{T_{sc}}.\frac{zT}{P} = 0.02827\frac{zT}{P}\left[\frac{ft^3}{scf}\right] \tag{22}$$

$$B_g^{min} = 0.02827.\frac{0.93.(147 + 460)}{2945} = 0.0054\ ft^3/\ scf$$

Values for the deviation (compressibility factor) and FVF for different reservoir pressures and ranges in the estimation (min, max, mean and optimal) can be found in Table 9 (below) as a function of projected pressure depletion and reservoir production in future. Temperature and pressure as a function of depth are calculated based on "normal" geothermal and hydrostatic pressure gradients (0.03 K/m (26^{O}C/km and 0.01 MPa/m, respectively). Further, it is assumed that porosity, bulk density and water saturation are independent of depth with the gas being pure methane with 1 Mol% of CO_2.

The formation gas volume factor (B_g) is measured in cubic feet per standard cubic feet and represents the volume occupied by "n" moles at specific reservoir pressure and temperature (P/T) to the volume of the same amount at standard conditions (stock tank in place). It includes the compressibility factor (z), which is a complex functions of pressure temperature and gas compositions that adjusts the ideal deviation (PVT) factor to account for non-ideal conditions of the gas (formation pressure and temperature). The *z* factor represents the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same P/T conditions. It is a useful thermodynamic property for modifying the ideal gas law and account for real gas behavior. Ideal gases have value of z that equal 1, but for real gases the values can be either positive or negative depending on the intermolecular forces of the specific gas. If the gas is closer to the critical point the deviations from ideal conditions are larger. On the figure (Figure 43), it is presented the compressibility factor variations for different gasses at the same P/T conditions (upper) and the change of z (for methane) at given pressure but rising temperature. On the right part of the figure (Figure 43) the plot for the deviation factor with change in pressure is depicted, that is estimated for the mean Alum Shale reservoir pressure (7106 psi), with specified variables for gas gravity – 0.7; temperature of 275 °F; and methane as a gas composition with 1 Mol % of CO_2.

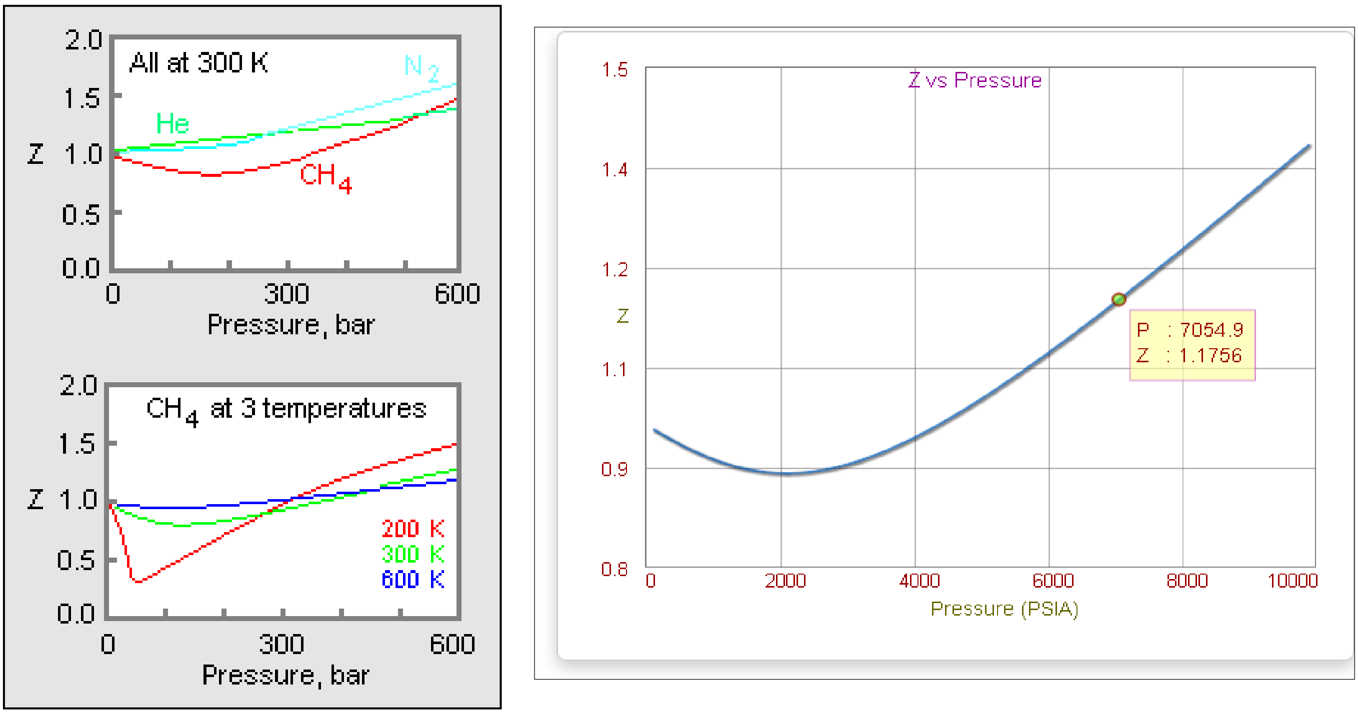


Figure 43 Gas deviation factor (compressibility) change in behavior of different P/T conditions for different gases (left) and plot diagram of CH4 compressibility factor for mean reservoir formation pressure of Alum Shale

All the values for the z factor can be traced in Appendix A, where for each burial depth and pressure fluctuation there is an estimated deviation from ideal conditions. Furthermore the following composite table (Table 9) represents the change of deviation factors for Alum Shale, with respect to pressure decrease and shallowing of the formation. The values for z at different conditions will be crucial for the calculation of cumulative gas (after hypothetical volumetric depletion).

Table 9 Calculated values for Z, FVF and cumulative production at different pressures inferring of different depths for Alum Shale reservoir

Range	P (psi)	Z	Bg ft^3/scf	Pressure after 1 month of production	Pressure after 2 months of production	Pressure after 1 year of production	Cumulative resource (theoretical)
Minimum	8300	0.76	0.0089	8050	11000	9800	-
Maximum	8702	1.10	0.0183				-
Mean	7106	1	0.0133				-
Optimal	2945	0.93	0.0110	2766	2500	500	8 Tcf

The determination of the deviation factor for other depth intervals of Alum Shale is calculated for different reservoir temperatures and pressures. If not calculated by thermodynamic plotting, if should be calculated from the critical properties of the gas composition and derived from the ideal gas law, which is the simplest equation of state (EOS):

$$PV_m = zRT =>, Z = \frac{PV_m}{RT} \qquad T_r = \frac{T}{T_c} \text{ and } P_r = \frac{P}{P_c} \tag{23}$$

The limitation of the equation (Equation 23) above is that the Z value is not constant for different gases or at different P/T conditions. The value for Z tends to 1 when the pressure is approaching surface conditions (1 bar), where all gases have ideal behavior. At intermediate pressures, the deviation factor is less than 1, due to intermolecular forces of attraction that decrease the actual volume to less than the ideal one. Values greater than 1 are assigned to Z, when the pressure is extremely high and the actual volumes are greater than the ideal values, due to intermolecular repulsive forces. Any pure gas at the same reduced temperature and reduced pressure (T_R and P_r) should have the same Z factor (Equation 23). Critical temperature and pressure (T_c and T_p) of gas are characterized for a single gas and stand for the impossibility of liquefying the gas beyond certain maximum temperature and the minimum pressure required to liquefy a given gas at its critical temperature. Other EOS for calculation of Z is the van der Waals equation and Redlich-Kwong. Errors in compressibility factors can occur at high concentrations of non-hydrocarbon gases (such as H_2S or CO_2), where the deviation from the real value can be up to 10%.

Step 1.3: Calculation of free initial gas in place (GIP) and estimating the resource concentration

PVT reservoir engineering equations and conversion factors are applied for the estimation of free GIP:

$$GIP^{min} = \frac{V_b^{min}(1 - S_{wmin})}{B_{gmin}} = \frac{8.57\ x\ 10^{11}\ x\ (1 - 0.85)}{0.0089} = \mathbf{14\ Tcf}$$

$$GIP^{max} = \frac{V_b^{max}(1 - S_{wmax})}{B_{gmax}} = \frac{1.3\ x\ 10^{13}\ .\ (1 - 0.20)}{0.0183} = \mathbf{568\ Tcf}$$

$$GIP^{mean} = \frac{3\ x\ 10^{12}\ .\ (1 - 0.50)}{0.0133} = \mathbf{112\ Tcf}$$

$$GIP^{opt} = \frac{3\ x\ 10^{12}\ .\ (1 - 0.80)}{0.0110} = \mathbf{54\ Tcf}$$

Where:

V_b^{min} – bulk prospective area (for different ranges of the assessment) and B_{gmin} – formation volume factor, ft^3/scf

Step 1.4: Cumulative production prediction for free GIP in shale-gas reservoirs with decreasing pressure

Even though, a projection for the actual production stream and the intensity of certain shale reservoir (number production wells, pressure drop, drainage area of single well and EUR) cannot be given before any commercial outcome of gas is received, the cumulative production will be forecasted only for the free GIP. The long-term extraction process in unconventional reservoirs is minimized to a few years time basis, where desorption of adsorbed gas in the micro and nano-pores derive the exact prediction of volumes that might be received at the wellbore after the completion stage. According to the pressure drops (**isothermal calculation**) in the formation, the cumulative resources are estimated as follows:

Gas state equations present the dynamic equilibrium between gas pressure, volume and temperature and their relationship that can be shown by the PVT curve of the area studied. For the different pressures of the formation the FVF are calculated, with calculation of the cumulative resource only for the minimum projection (Table 9):

- Initial FVF (at 2945 psi) - **0.0089 ft^3/ SCF**
- Gas FVF after 1 month of production (at 2766 psi) – **0.0091 ft^3/ SCF**
- Gas FVF after 2 months of production (at 2500 psi) – **0.0093 ft^3/ SCF**
- Gas FVF after 1 year of production (at 500 psi) – **0.0098 ft^3/ SCF**

This yields:

- Initial (de-risked) free GIP_{min} = **14 TCF**
- GIP_{min} after volumetric depletion to 2766 psi = **13 TCF**
- GIP_{min} after volumetric depletion to 2500 psi = **9.2 TCF**
- GIP_{min} after volumetric depletion to 500 psi = **7.3 TCF**

This means that the gas reserve (cumulative) by volumetric depletion to 500 psi is:

$$Cumulative\ GIP = GIP\ (initial) - \ GIP\ (500\ psi) = \ 1.4\ x\ 10^{13} - \ 7\ x\ 10^{12} = 7\ x\ 10^{12} = \boldsymbol{7\ Tcf}$$

$$Recovery\ factor\ (RF) = \frac{7\ x\ 10^{12}}{14\ x\ 10^{12}} = 0.20 = \mathbf{20}\ \%\ (\underline{Theoretical\ and\ not\ final\ value})$$

Bear in mind that the free GIP is taken as an initial value, before it is risked and before any success factors and adsorption gas is applied to it. This resource (14 TCF) is just a raw estimation of the concentration of bulk gas, without accounting for further factors in the assessment. Below, the assessment will concentrate on the sorbed gas estimation and technically recoverable resources. The aim of this practical calculation of cumulative resources is to show the relationship of the resource produced with volumetric (pressure) depletion (Figure 44). The method is adopted from conventional resources, thus why the values for GIP and RF should not be treated as realistic but only theoretical. Further in the calculation the final TRR of shale gas resource will be estimated.

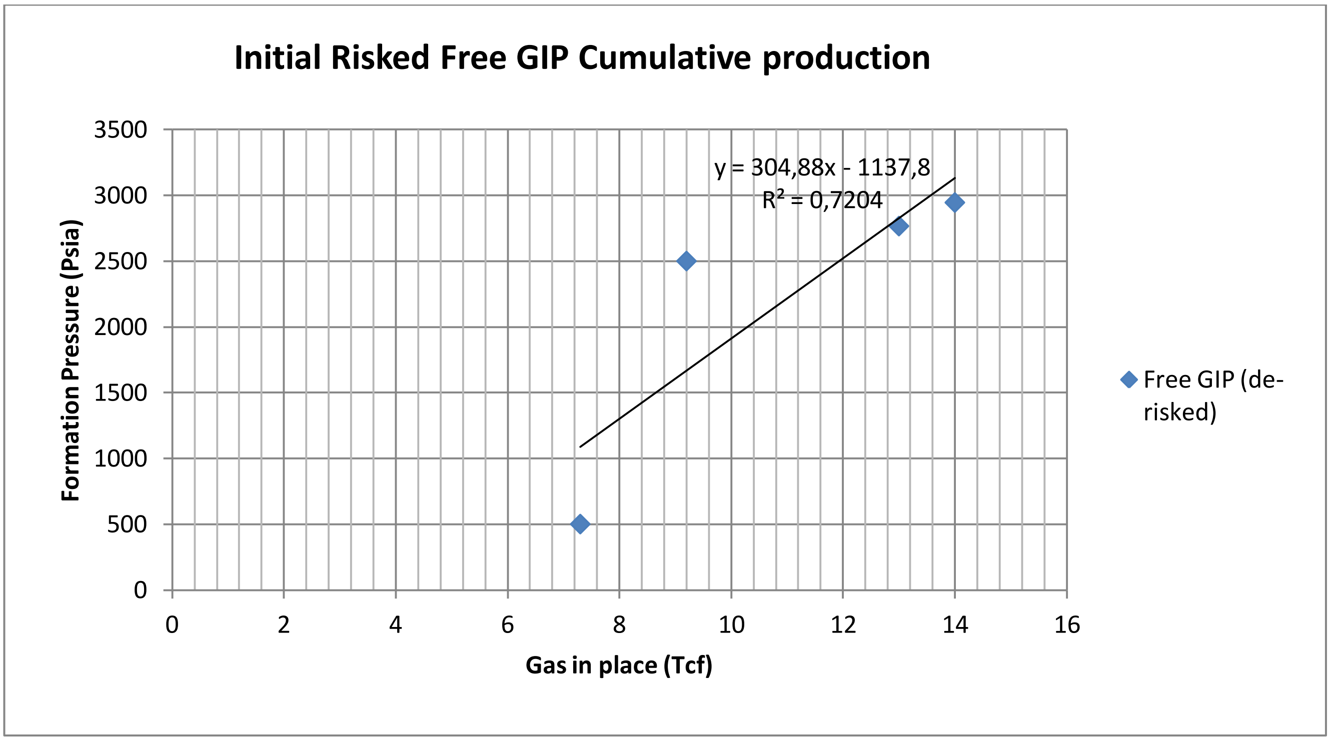


Figure 44 Linear trend of theoretical shale gas resource volumetric depletion during production (by-calculation)

Two main conclusions derive from the trend seen (Figure 44) – first as pressure drops abruptly (3000 to 500 psi) the gas received at the wellbore will equal 1/3 of the total resource, if the field is exploit simultaneously, and second, if we have to adjust the values for shale gas, which requires several hundreds of wells for extracting the same portion (1/3) of the resource, such a downward slope will be achieved in a month's time-basis. The cumulative resources calculated above, represent a huge number (7.3 TCF - unrealistic for unconventional shale gas resources), because the estimation is usually adopted from conventional reserves.

Step 2: Estimation of Adsorbed Gas In-place for Alum Shale

This calculation will differ from the EIA/ARI, 2013 method, because it will include several optimizations. As the characteristics for a typical shale gas log response is very high gamma ray activity, high resistivity, and low bulk density, this is always a function of the high concentration of kerogen. Kerogen`s density ranges from 0.95 to 1.06 g/cm^3 which affects the bulk density of the rock. Furthermore, kerogen can create reducing environment that leads to precipitation of uranium (Lewis et al., 2004), and thus result in high gamma-ray response. This infers that the amount of the adsorbed gas is a function of kerogen content and temperature. Based on the latter considerations, quantification of the kerogen content (typically TOC) is needed in shale gas resource calculation. Because kerogen is derived usually from sonic or density log, precise quantification is hard, due to variable mineral content and matrix property in shales. The governed gamma-ray log from the kerogen quantity needs to be accounted for with a correction for the volume of the kerogen in-place with actual TOC data. Kerogen for Alum Shale is assumed to be 9-11 % (analogue from Barnet Shale). After the volume is calculated for kerogen, the adsorbed gas volume will be linked to the converted values of TOC.

The following equation (24) applies for the conversion, where the factors used are for other impurities in kerogen (oxygen, hydrogen, sulfur) (factors are listed in Appendix A):

$$TOC = \frac{\phi_{ker} * \rho_{ker}}{\rho_b * k} = \frac{10*1.2}{2.3*1.2} = 4.34\ lbf/lbf \qquad (24)$$

Where TOC is total organic carbon (lbf/lbf), ϕ_{ker} is the kerogen volume (vol/vol), ρ_{ker} is the kerogen density (g/cm^3), and k is the kerogen conversion factor (usually around 1.2).

The values for the gamma ray activity for Alum Shale are derived from the Terne-1 log (Figure 47), where the values range from 480 to 1200 gAPI (mean 850gAPI), and TOC range of 14 wt%.

The adsorption kinetics and relationship of the Langmuir adsorption equation can be extended for the multiple compositions (several different compositional fractions of gases – e.g. CO_2, N_2, CH_4, C_2H_6, etc.). In order to calculate a shale methane resource completely composed of only CH_4, the common form of the equation is used:

$$\mathrm{V_{ad}}(G_c) = \frac{V_{LCH_4} P}{P + P_{LCH_4}} \quad \textbf{and} \quad \mathrm{GIIP\ (ad)} = \mathbf{A} * \mathbf{h} * \rho * G_c \quad \textbf{or} \quad \mathrm{GIIP(ad)} = \mathbf{V_b} * \rho * G_c$$

In which, the G_C is the gas content (volume of gas/weight of shale) given by the Langmuir equation (left) with V_L (Langmuir volume at infinite pressure) and P_L (Langmuir pressure with 50% of the gas at infinite P has been desorbed), and the A – area, h – thickness and ρ – density of the shale formation.

Where are laboratory measurements of core samples, the Langmuir equation on the left can be directly implied to calculate G. As in the case of the report, values were taken from Gasparik et al. (2013) report[1], and shown in Appendix A. The multi-compositional gas adsorption equation is derived by adding two other gaseous phases (m=3), where the adsorbed volume of CH_4 will be influenced by the fractions of other gases:

$$V_{CH_4} = \frac{V_{LCH_4} P_{CH_4}}{P_{LCH_4}\left(1 + \frac{P_{CH_4}}{P_{LCH_4}} + \frac{P_{CO_2}}{P_{LCO_2}} + \frac{P_{N_2}}{P_{LN_2}}\right)}, \quad \text{and} \quad \mathrm{V_{ad}} = \mathrm{V_{CH_4}} + \mathrm{V_{CO_2}} + \mathrm{V_{N_2}}$$

The change in gas storage capacity with depth for dry and 80% water saturation (Sw) and the relationship between the different gaseous states for Alum Shale are depicted below (Figure 45). The shaded areas correspond to sorption capacity calculations of different Alum shale samples done by Gasparik (2013), which have different TOC (4.4-9.0%). Also the canister desorption test done by Pool et al. (2012) is represented as a black cross. Water saturation (S_w) is reversely proportional to gas storage capacity. As water in the pore and matrix system increases, sorption capacity decreases.

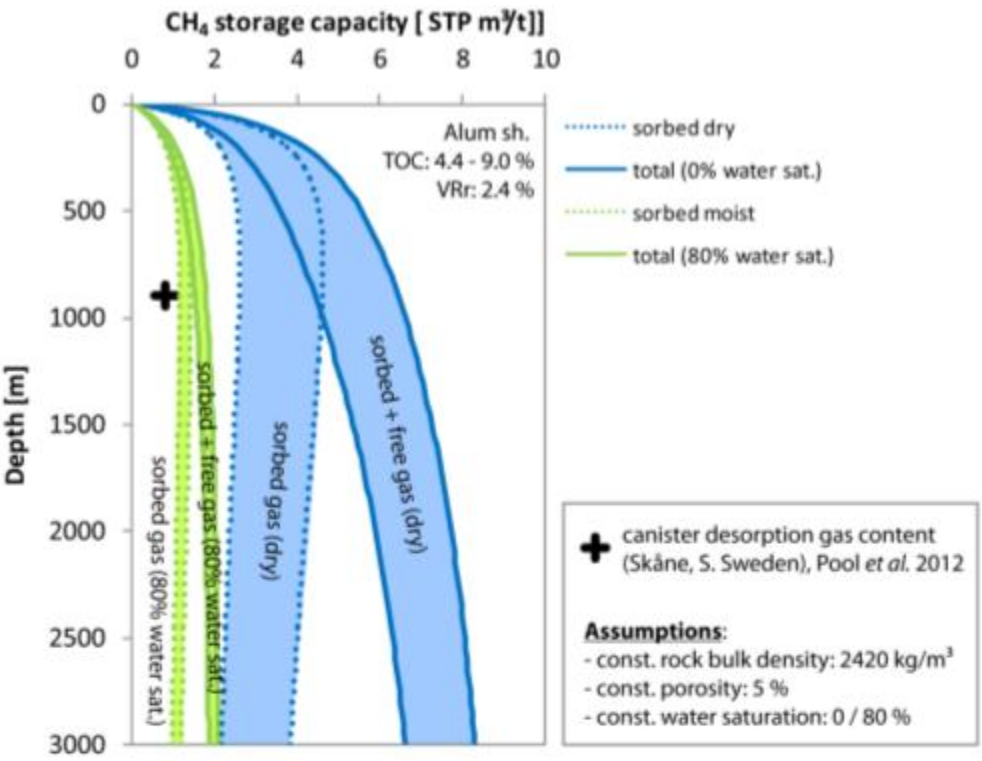


Figure 45 Methane excess sorption and total storage capacity as a function of depth calculated based on the excess sorption data for Alum shale (reported by Gasparik, 2013). The blue and green shaded areas correspond to the scenario of completely dry reservoir and reservoir with 80% water saturation, respectively. The gas content reported by Pool et al. (2012) for the Alum Shale in Scania is shown as a comparison (black cross) (Gasparik et al., 2013)[1].

This is why other factors should be implemented, such as reservoir parameters, or competitive storage capacity of adsorbed gas. This report assumes 20% water saturation (S_w) content in the pore system of Alum Shale for its best case, and 50% for the mean estimated value.

So with the assumption that the reservoir is mono-gaseous, and only methane saturated, the following calculations are performed for the adsorption isotherm:

$$V_{ad^{min}} = \frac{V_{LCH_4}P}{P+P_{LCH_4}} = \frac{20\,x\,2945}{2945+432} = \mathbf{17}\ \frac{\mathbf{scf}}{\mathbf{ton}} \tag{25}$$

$$V_{ad^{max}} = \frac{63\,x\,8300}{8300+700} = \mathbf{58}\ \frac{\mathbf{scf}}{\mathbf{ton}}$$

$$V_{ad^{mean}} = \frac{36\,x\,7106}{7106+435} = \mathbf{33}\ \frac{\mathbf{scf}}{\mathbf{ton}}$$

$$V_{ad^{opt}} = \frac{32\,x\,8702}{8702+420} = \mathbf{30}\ \frac{\mathbf{scf}}{\mathbf{ton}}$$

V_{ad}, which is equivalent to the G_C stands for adsorbed gas content and represents the volumetric quantity of sorbed gas in a ton of net shale (scf/ton; where 1 mmol/g = 22.71 std.m^3/t = 802.03 scf/ton).

The Langmuir isotherm is calculated at exact TOC and temperature, where correction for the logging procedure should be implemented for the range of the two variables. Constants *c3* and *c7* were applicable for coal bed methane and adopted from the adsorbed gaseous calculation in CBM. The following equations (26) account for the Langmuir temperature and pressure correction:

$$V_{lt} = 10^{(-c3*(T+c4))} = 10^{(-0.0027*(135+160))} = 0.15\ scf/ton \qquad (26)$$

$$P_{lt} = 10^{(c7*(T+c8))} = 10^{(0.005*(135+328))} = 200\ psi$$

$$c4 = \log V_l + (c3 * T_i) = 160 + (0.0027 * 65) = 160$$

$$c8 = \log P_l + (-c7 * T_i) = 330 + (-0.005 * 65) = 328$$

Where:

- V_{lt} - Langmuir volume at reservoir temperature (scf/ton)
- Pl_t - Langmuir pressure at reservoir temperature (psi)
- c3 - 0.0027
- c7 - 0.005
- T - reservoir temperature (°C) – 135°C (own investigation)
- T_i - isotherm temperature (°C) – 65°C for excess sorption (Gasparik et al., 2013)

In case to obtain values for the **log**P_l the following thermodynamic sorption equations should be implemented:

$$p_L = \frac{\Delta H}{RT} - \frac{\Delta S^0}{R} + \ln p^0 \qquad (27)$$

Where ΔH is the enthalpy of sorption, that equals the isosteric heat of adsorption q_{st} but with a negative sign (ΔH = -q_{st}); ΔS_o is the molar entropy of sorption and p^0 = 1 bar is the pressure at the perfect-gas reference state (Myers and Monson, 2002). Values for the logarithm of the Langmuir Pressure were taken from the latest results from Gasparik et al.,2013, with a mean value of ln(p_L) = 2.28 MPa or 330 psi (Figure 46). For the Langmuir volume and excess sorption an ln (V_L) = 0.2mmol/g (160 scf/ton) is derived (Gasparik et al., 2013).

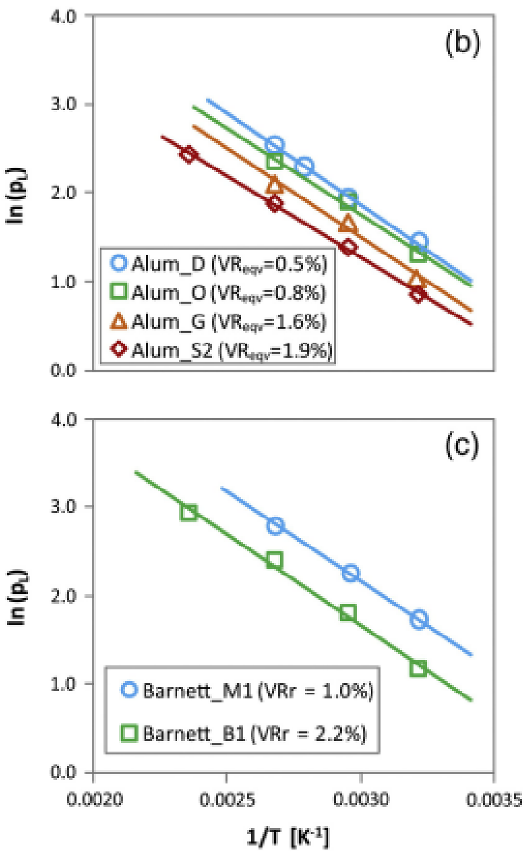


Figure 46 Linear plots of the logarithm of Langmuir pressure (pL) versus the inverse of the temperature 1/T. The values were obtained from Gasparik et al. 2013 and fitting the equation above (Equation 27) to the isotherms measured at different temperatures (Gasparik et al., 2013)

A necessary correction for TOC is needed, because the gas can only adsorb onto kerogen, the relationship is shown in the equation (28) below:

$$V_{lc} = V_{lt} * \frac{TOC_{lg}}{TOC_{iso}} = 0.15 * \frac{9}{7} = 0.19\ scf/ton \qquad (28)$$

In which, V_{lc} is the Langmuir volume corrected for the reservoir temperature and TOC (scf/ton); TOC_{iso} = total organic carbon from isotherm (wt %); and TOC_{lg} = total organic carbon from log (wt %). Values for TOC_{lg} are obtained from the log Terne-1 where the TOC maximum value is 14% and a mean of (9%) (Figure 47)

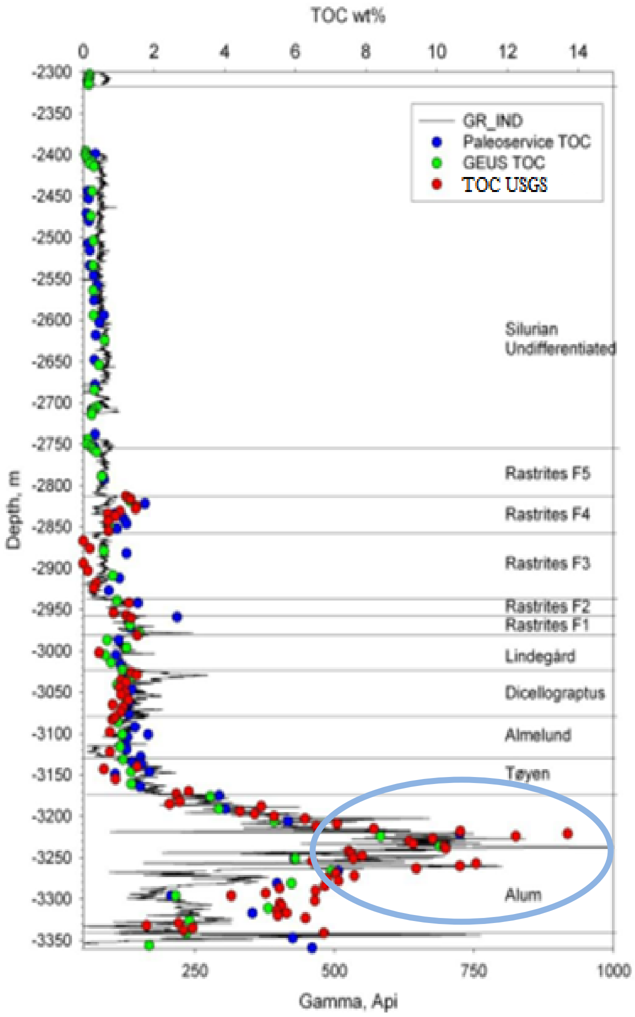


Figure 47 Gamma-ray response for a 1000 m interval of the well Terne-1 in the Kattegat area (Gautier et al., 2013)

This combination of procedures followed leads to correction from the value of V_{ad} obtained above (Equation 25). Due to range projections, only the mean value will be corrected in case to implement the whole systematical approach. This yields the following expression:

$$V_{ad}^{mean\ and\ opt}(Gc) = \frac{V_{lc}*P}{(p+P_{lt})} = \frac{0.19*7106}{(7106+200)} = 0.18\ scf/ton \qquad (29)$$

This result shows the crucial correction parameters that should be used in any isothermal calculation for adsorbed gaseous state in a shale reservoir. That infers that the mean and optimal value for V_{ad}, respectively for the in-place resources, will differ significantly from the other, because of corrected TOC and reservoir isothermal adsorption, and thus is deemed as the most realistic one.

In order to convert the all the values (min, means, opt and max) value to gas concentration, the density (ρ) of the shale (Table 8) along with area and thickness (Appendix A) are added to the value:

$$GIP_{ad}^{min} = V_{ad^{min}} .\rho. V_b^{min} = 17\ x\ 2.3\ \ x\ 8.57\ x\ 10^{11} = 33\ Tcf \qquad (30)$$

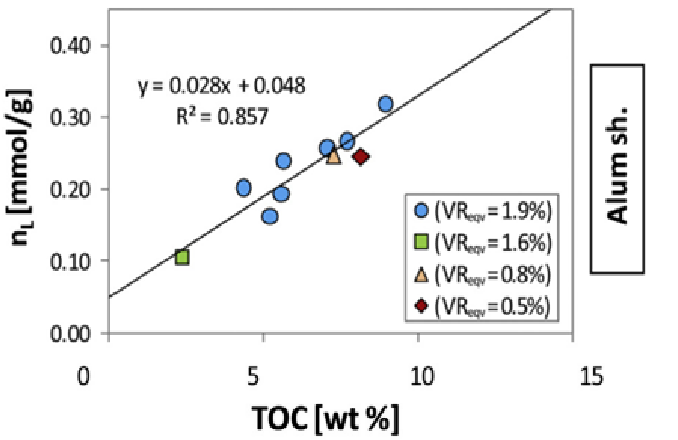
$$GIP_{ad}^{max} = V_{ad^{max}} \,.\, \rho . V_b^{max} = \; 58 \; x \; 2.6 \; x \; 3 \; x \; 10^{12} = 452 \; Tcf$$

$$GIP_{ad}^{mean} = V_{ad^{mean}} \,.\, \rho . V_b^{mean} = \; 0.18 \; (corrected) x \; 2.5 \; x \; 3 \; x \; 10^{12} = 1.3 \; Tcf$$

$$GIP_{ad}^{opt} = V_{ad^{opt}} \,.\, \rho . V_b^{opt} = \; 0.18 \; (corrected) x \; 2.3 \; x \; 3 \; x \; 10^{12} = 1.24 \; Tcf$$

Where the area (A) is initially in acres-foot, and then converted from acres to square miles (640 acres per square mile), density (ρ) is in g/cm^3, bulk reservoir volume (V_b) in cubic feet, and V_{ad} in scf/ton.

Depending of the TOC concentration in different parts of the formation and the rank of maturity, adsorbed gas can uptake significant quantity of the shale`s pore space. An interactive model, with probable distribution of adsorbed gas along with its proportions in the reservoir will be the outcome of the adsorption correction procedure. The reasons for different gaseous state in different sections are explained below. For Alum, preliminary it is expected free gas to dominate, due to factors such as, less vitrinite (maceral not VR_o) quantity in the shale, high temperature ranges (deep burial), which causes faster kinetics and endothermic desorption, and finally the less moisture quantity in the Cambro-Ordovician reservoir.



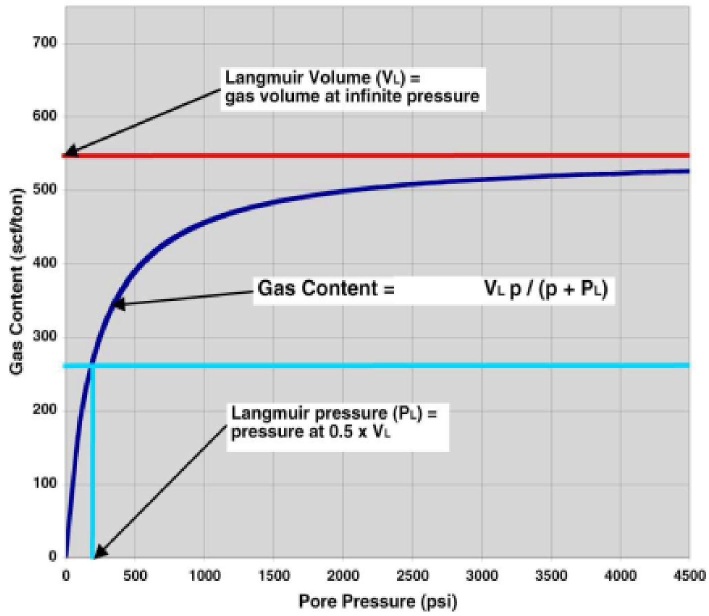


Figure 48 Maximum Langmuir capacity (VL= nL) as a function of TOC for dry Alum Shale samples (Gasparik et al. 2013) (left) and a typical Langmuir isotherm results (right) Curved lines define the equilibrium between adsorbed and free gas as a function of reservoir pressure at the isotherm conditions.

The Langmuir volume and Langmuir pressure for the methane sorption are a function of the organic richness and the maturity of the formation, which was recently developed with adding the influence of moisture, porosity, other non-hydrocarbon gases, shale matrix type and clay adhesive properties on the V_L and P_L (Gasparik et al. 2013). It should be clarified, that if the TOC of the shale is lower, than the adsorbed gas content will be also smaller, and vice versa (Figure 48). That is why the values of the Langmuir adsorption isotherm are taken at average TOC for the formation (7%), from the paper[1] of Gasparik et al. (2013).

The gas content (scf/ton) and sorption isotherm values are usually measured in laboratories from core samples. The gas content for Alum Shale or the total gas storage capacity equals 75 scf / ton, but the adsorption isotherm capacity has been calculated to be 30 scf / ton, according to Pool et al. 2012. This concludes that the reservoir is probably undersaturated. For the calculation undertaken in this report, a fairly moderate range of adsorbed gas content (17-58 scf/ton) has been estimated using new values for the adsorption isotherm, with the correction parameters. In U.S. as an example the ratio between adsorbed and free gas is in the vicinity of 60:40 to 10:90 (Jarvie, 2012).

Step 3: Estimation of Total risked and technically recoverable GIP

The free and adsorbed gases in place (GIP) are finally combined to calculate the resource concentration (Bcf/mi^2), as can be found in the procedure of Chapter II. The conversion factor of 640 acre per square mile is applied on both free and adsorbed GIP in case to derive the gas concentration in similar units (Bcf/mi^2).

The total gas in place (GIP) (Bcf/mi^2) = Free gas (free GIP) + Adsorbed gas (adsorbed GIP)

Where the Total GIP, Free and Adsorbed GIP are all expressed in units of Bcf/mi^2

Two judgmentally success/risk factors are added to estimate the risked GIP in the prospective area of Alum Shale Onshore AU, which combined form the Composite Success Risk Factor:

- Play Success Probability Factor – this factor identifies the portion of sweet spots in a prospective area of shale gas resource. Alum Shale is still not under development which cannot yield a factor of 100%, like in other U.S. shale basins. On the other hand, the Danish Alum Shale has sufficient geological data from several wells and cannot be also considered as speculative shale formation with Play Success Factor of 40%. Average factor of 70% is assigned (Appendix A), with which to risk the in-place resources, but however as exploration wells are drilled and tested, Alum Shale`s gas reservoir properties are further revealed, and the factor will change.

- Prospective Area Success (Risk) Factor – takes into account concerns that can relegate a portion of the AU area to be unfavorable or not profitable for production of shale gas. Alum Shale reservoir is mainly situated beneath the Variscan unconformity in a complex geologically tilted fault blocks. This high structural setup may hinder problems in the completion stage`s execution, which will result in unsuccessful production. However, the shale reservoir experiences increase of thermal maturity towards the Caledonian front, and Alum is known to lack of low thermal maturity in its prospective area. Finally, the factor excludes the marginal areas of the AU, with low TOC quantity. Alum Shale was assigned upon the mentioned considerations to have 60% in average play area success (Appendix A).

Composite Success Risk Factors for different probabilities of the gas resource potential (only onshore AU) in Alum Shale are depicted in the table below (Table 10).

Recovery factor for unconventional gas fields is established for the de-risked GIP and it is preceding the value of recoverable reserves. For the Alum Shale the recovery efficiency factor varies between 5% and 25% (average 15%), because the clay quality is in moderate proportions, the formation is deemed to have high geologic complexity with expected favorable reservoir properties, and overpressured reservoir. Although the shale reservoir is not expected to contain any hydrocarbon liquids (condensate, oil), but only thermogenic gas (methane), it might store some small quantities of non-organic gases.

Technically recoverable resources (TRR) are estimated by incorporating several geological inputs and efficiency factors. Geological information and data, such as bulk mineral composition for favorability when applying hydro-fracturing techniques, presence of natural micro-fractures in-situ, areas without intense faulting that can interrupt laterals, average elastic modulus and stress-strain ratio for the shale, and ΔP between formation pressure and reservoir bubble point pressure (at which liquid turns into vapor with pressure drop).

If Alum Shale is developed and produced, the initial starting threshold of horizontal well completions will comprise of more than 10 stages of hydro-fracturing along almost a kilometer long lateral. Due to this advancement in technology, the recovery efficiency and prospective area are constantly increasing. The starting point for Barnett Shale well completions were at less than 600 m horizontal wells with only 5 stages of multi-fracturing, which accounted for not more than 25% of recovery factors, where as now more than 15 multi-stages are executed per clustered section.

8.3. Results and comparison with previous assessments

The calculation procedure in this report uses imperial units, which are not converted to SI (metric) units, because of the assessment approach of previous calculation procedures that originated mainly from the United States. The step-by-step volumetric resource estimation for shale gas resource of Alum Shale, was done in full scale for the onshore resource in a preliminary defined prospective area, taken from the public literature, and modified to some extent. This resulted in three key assessment values:

- **GIP Concentration Content (Total GIP) -** in Bcf/mi^2
- **Risked GIP** – given in billion cubic feet (BCFG or Tcf) for Alum Shale calculations;
- **Risked Recoverable Gas** – reported in BCFG or Tcf, and representing the technically achievable resource to be produced.

The following tables (Table 10, 11) will summarize the total (Onshore and Offshore AU) resource availability in Alum Shale, with the additional estimation of the Offshore AU, by repeating the same calculation procedure, for a different prospective area and reservoir parameters (Appendix A).

Table 10 Onshore AU shale gas resource and reserves for the Danish Alum Shale

Alum Shale gas potential in the Onshore Assessment Unit (OAU)				
Probability	Onshore area (mi^2)	Total gas content Estimates (Bcf/mi^2)	Composite Success Risk Factor (Area + Risk)	Total Risked Gas-in Place (TCF)
Min P10	4687	73	10 %	34
High P10	**6250**	**1,593**	**70 %**	**6969**
Mean P50	5325	176	50 %	468
Optimal P90	**4800**	**55.3**	**30 %**	**79.2**

Probability	Risked Gas-in Place (TCF)	Recovery Factor (%)	Technically recoverable reserves (TCFG)
Min P10	34	5%	1.7
High P10	**6969**	**25%**	**1742**
Mean P50	468	15%	70
Optimal P90	**79.2**	**10%**	**7.9**

*OAU – onshore assessment unit, TCFG, trillion cubic feet of gas;

The recoverable reserves for the Onshore AU prospective area were estimated to an optimal value of **7.9 TCF (P90)** of shale gas from Alum Shale on the onshore territory of Denmark. The derived number is intensively rigorous and assumed as mean conservative resource abundance. The GIS model for the prospective area, which is based on depth, maturity, TOC and thickness properties of Alum, adopted by Gautier et al. 2013 (USGS), provided the needed delineation of the area with which to assess the resource.

Table 11 Offshore AU shale gas resource and reserves for the Danish Alum Shale

Alum Shale gas potential in the Offshore Assessment Unit (OFAU)				
Probability	Offshore area (mi^2)	Total gas content Estimates (Bcf/mi^2)	Composite Success Risk Factor (Area + Risk)	Total Risked Gas-in Place (TCF)
Min P10	5843	110	10%	64
High P10	**7840**	**2,612**	**60%**	**12286**
Mean P50	6140	295	40%	724
Optimal P90	**6713**	**279**	**30%**	**146**

*OFAU – offshore assessment unit, P90 – represents a 90-percent chance of at least the amount tabulated

Probability	Risked Gas-in Place (TCF)	Recovery Factor (%)	Technically recoverable reserves (TCFG)
Min P10	64	5%	3.2
High P10	**12286**	**25%**	**3071**
Mean P50	724	15%	107
Optimal P90	**146**	**10%**	**14.6**

*OFAU – offshore assessment unit, P90 – represents a 90-percent chance of at least the amount tabulated

The gas available in the Offshore AU was calculated to be **14.6 TCF (P90, Optimal)**, which is around 45% more than that in the onshore AU of Alum Shale. This infers from the lower success area factors in the offshore unconventional production. Even though, the area of the offshore unit incorporates twice as much more reservoir bulk volume, the reduction with the low area successes risk factor (30%) provides substantial cut-off of the resources. The area has assigned such factors because of limited and low probability of future exploration of unconventional gas in the offshore of Denmark.The total resource base in Alum Shale for the bulk shale gas present in the reservoir is given in the following summary table (Table 12) and depiction graph:

Table 12 Total risked GIP and OFAU and OAU TRR of shale gas from this assessment for Alum Shale

Alum Shale TPS Technically Recoverable gas potential and assessment results (OFAU and OAU)				
Probability	Total Risked GIP (BCFG)	Onshore Technically Recoverable Reserves (BCFG)	Offshore Technically Recoverable Reserves (BCFG)	Total Technically Recoverable Reserves (TCF)
Min P10	98	1.7	3.2	4.9
High P10	19255	**1742**	**3071**	4813
Mean P50	1192	70	107	177
Optimal P90	226	7.9	14.6	22.5

*BCFG, billion cubic feet of gas, TCF – trillion cubic feet; TPS – total petroleum system, GIP, gas in place; OFAU – offshore assessment unit

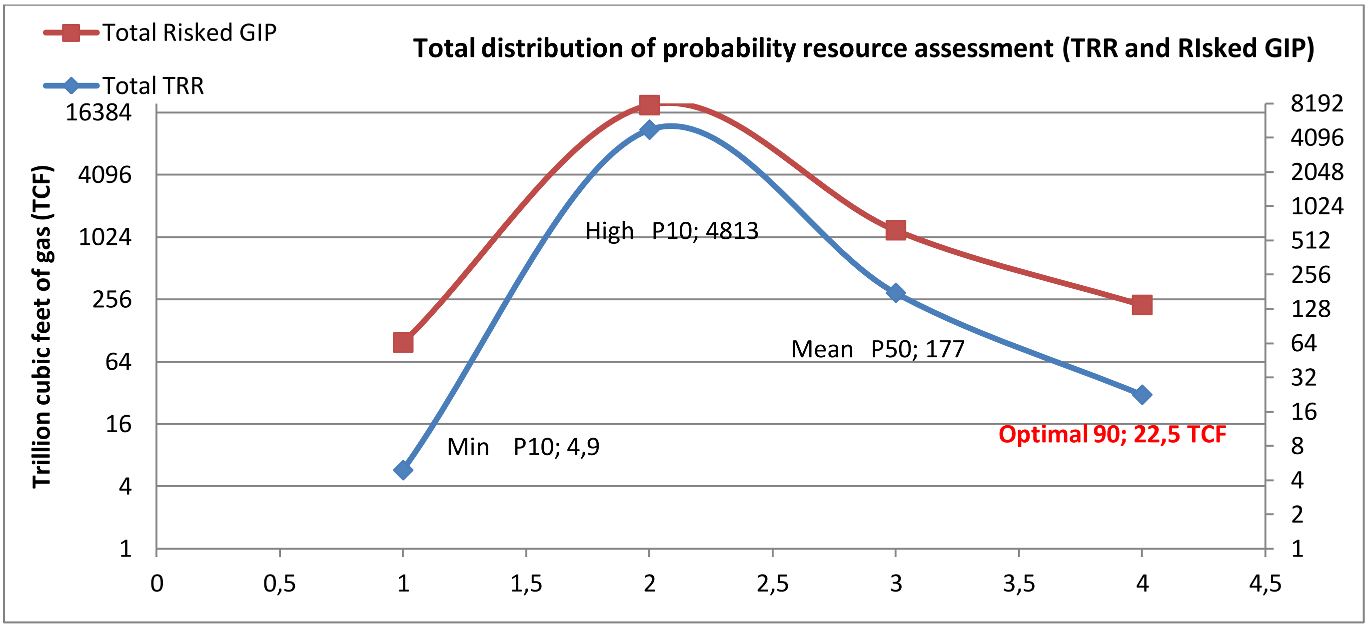


Figure 49 Probability range distribution of GIP and TRR resources in Alum Shale – Denmark

Total free and adsorbed gas ratio, proved to be around 55:45, for the uncorrected values (maximum and minimum projections).

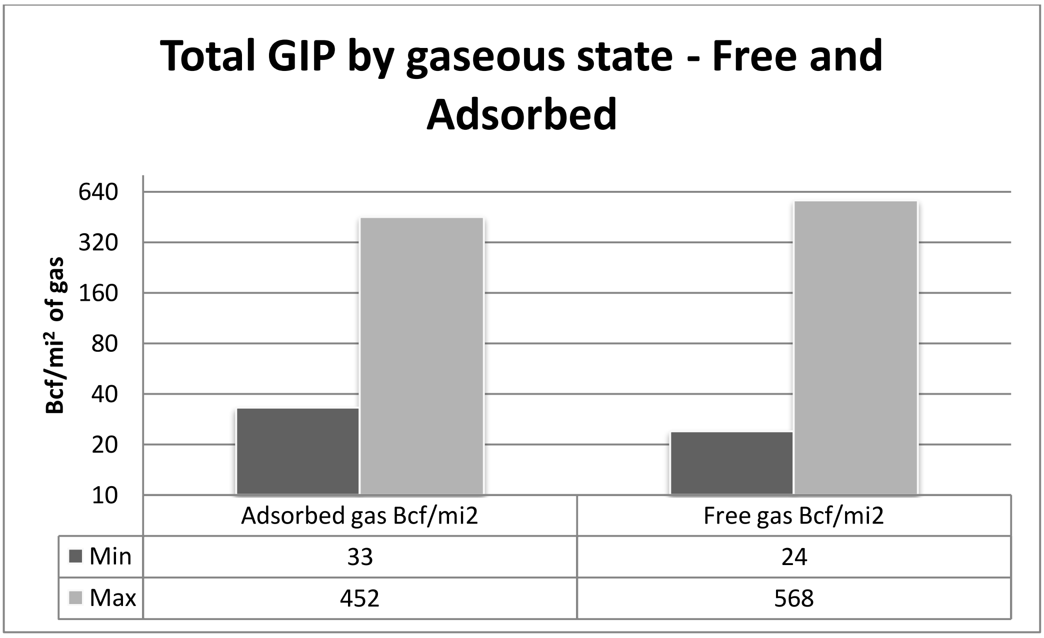


Figure 50 Proportions of adsorbed and free gas in Alum Shale – Denmark given in Bcf/mi2

The traditional calculation model for continuous accumulation by the volumetric approach, associates many uncertainties. The combination of geologic parameters (area, porosity, thickness), thus are combined with results for Alum Shale from the less difficult to model FORSPAN assessment of USGS (Gautier et al., 2013). This type of modeling considers an accumulation as a collection of oil and gas charged cells (tested or untested). The cell itself confines in an area that equals to the drainage area of a single well.

For Alum Shale, according to the results of USGS report[1] (Gautier et al., 2013) for their prospective area and recoverable resource, the mean/mode EUR is **0.492 BCFG** for the sweet spots (35% of the area delineated), with average well drainage area of **160 acres** (0.25 mi^2). The volumetric method parameters and the non-volumetric empirically well production of FORSPAN are the two methods combined to treat the reservoir data. Still, the untested cells in Alum Shale reservoir for this model (Gautier et al., 2013) are dominant, and wells with low EUR will be further dismissed or accounted as dry holes. It has been concluded the following estimation for the area:

- Total mean prospective area in the TPS – **8738991 acres**
- Onshore AU area – **3408324** acres and Offshore AU area – **5330667** acres
- Sweet spot area (mean 20%) – **1747799 acres**
- Area outside the sweet spots – **6991192 acres**

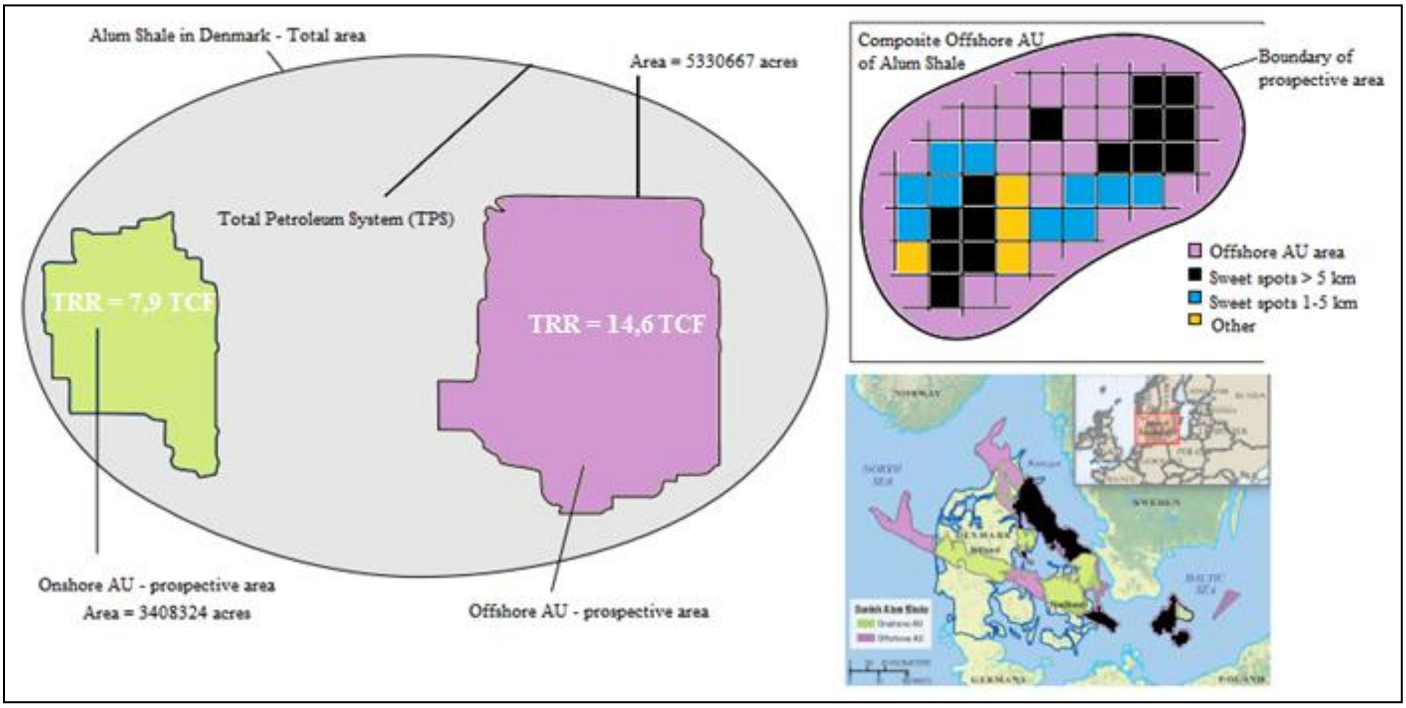


Figure 51 Composite depiction of Alum Shale prospective area, total petroleum system (TPS) and offshore AU prospective area boundary. Black squares and spots constitute for main offshore future exploration and production area (incremental modification, after Gautier et al. 2013)

With the obtained knowledge for the adsorption mechanisms and desorption characteristics researched in Chapter I, an interactive depiction based on several geological models was build (Figure 52). The scheme represents the proportion of the free and adsorbed gas in different sections of the prospective area of Alum Shale in Denmark. It consists of iso-reflectance lines on Danish territory, which controlling factor (maturity) defines the distribution and portions in the shale reservoir between the different gas states. Furthermore, the geological mode adapted and reallocated was the EGS-USGS GIS model (Gautier et al., 2013, Schovsbo et al., in press), with some of the polygons provided or found in the technical literature. Those include the overlapping of several maps such as, the adjustment for uplift in Late Paleozoic based on the thickness of Lower Paleozoic and depth map of Alum Shale of 1.5 – 5 km (Lassen & Tybo, 2012), maturity of Alum in the interval of more than 4% VR_o and for the iso-reflectance lines (with mapped areas of 7 km depth of the shale from the depth map of Lassen & Tybo, 2012), along with the composite polygon for the sweet and non-sweet spot distribution of Alum Shale in Denmark (Schovsbo et al., in press).

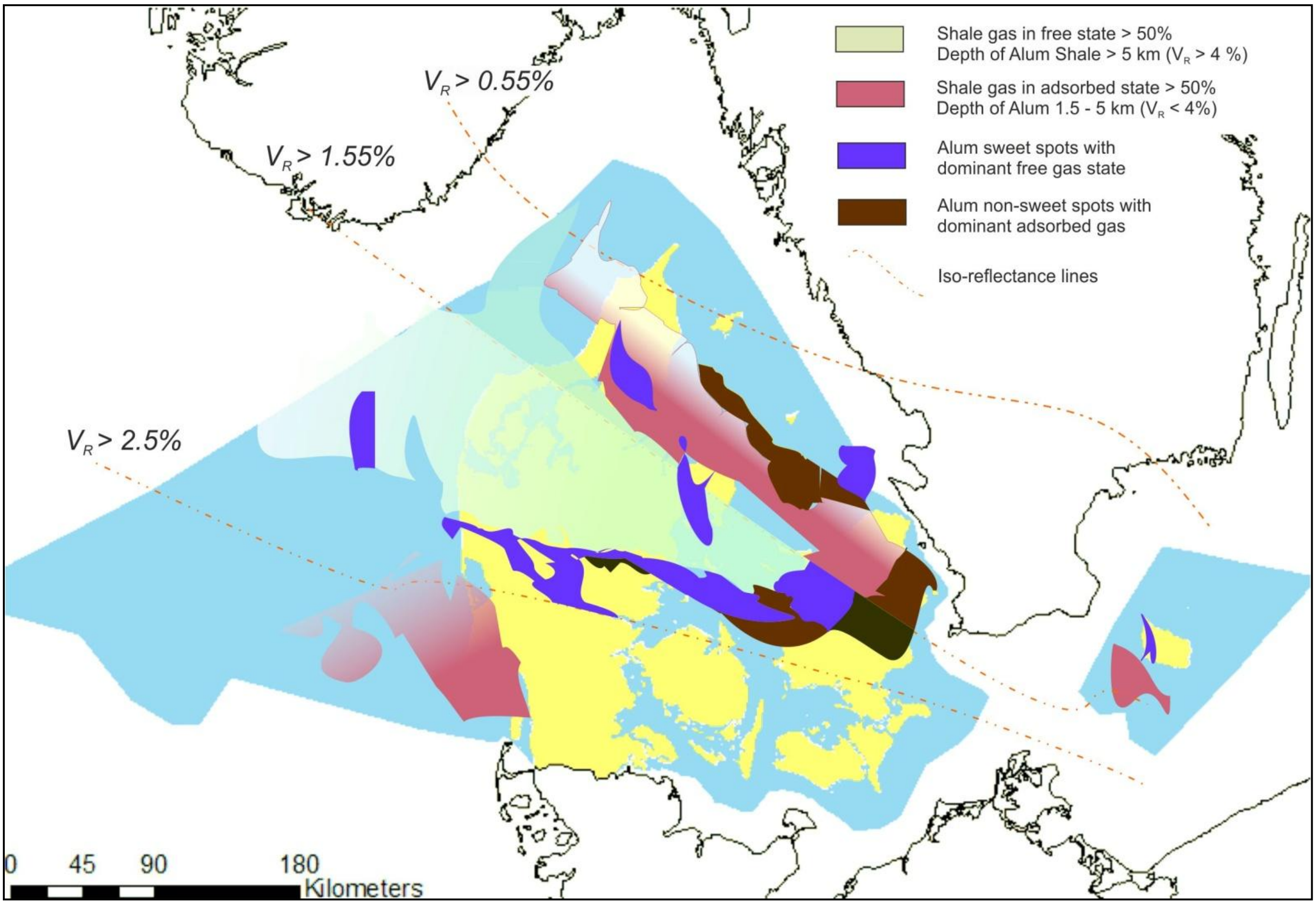


Figure 52 Schematic depiction of the proportions of free and adsorbed state shale gas in the prospective area and sweet spots of Alum Shale in Denmark (after Gautier et al. 2013)

The adsorption capacity of shale reservoirs to gas is affected not only by its nature, such as maturity or deformation but also by external factors such as moisture, temperature and pressure, which is why all should be accounted for (Ettinger et al., 1966).

The solid background of the model stands in the framework of the processes described on pore level. As Alum Shale is thought to have both adsorbed and free gas, with the theoretical proportion noted from the results above (Figure 50), in order to link the amount of both gas states and their proportions several relationships were used:

- Free gas dominates in deeper shales due to higher temperatures, which leads to activation in desorption, in endothermic reaction. The kinetic chemical reaction obtained in the adsorbed phase, provides the needed energy for it to overcome the adhesion and diffuse as free gas. This infers that the higher the temperature, the greater the quantity of free gas and less adsorbed state will be present. In this case, deeper shales are expected to have more free gas, due to higher reservoir temperature, whereas in shallow ones the adsorbed state will dominate. This is true, usually at identical pressure to the lower and higher temperature range, which isobaric conditions are not real in nature. However, further restrictions of this statement exist, where other parameters interact with this notion.
- Based on the competitive storage of organic and non-organic gases, CO_2 affects highly the amount of free and adsorbed gas. The fact that the Langmuir volume of shale has a linear relationship with the volatile component content, concludes that the volume decreases with increase of the volatile phase (CO_2, N_2, other hydrocarbon gases), and respectively the adsorbed gas quantity drops. That is another argument for the less amount of adsorbed gas with maturation of the source rock. This however, is not true for the organic matter pores, which host more gas phase, while maturity increases.
- As moisture content increases in shale, more effective sorption sites are occupied by water, and less are left for gas, which leads to low adsorption gas state in the volume of the rock.
- Two tendencies in of variation in the gas adsorption capacity of shale exist in shale maturity ranges: of $R_o < 4\%$, (Cainengzou et al. 2013) the sorbed capacity increases with maturity increase, whilst at $R_o > 4\%$ the adsorption capacity decreases as shale maturity rises. This led to delineating the R_o>4% points (light green) as shale gas with dominant adsorbed state.
- Vitrinite quantity can stimulate the adsorption capacity, with its increase, or if the shale is interbeded with coal. Vitrinite is thought to have the most powerful adsorption capacity (Cainengzou et al., 2013).
- Pressure and adsorbed volume capacity show a non-linear relationship, which cannot be simulated equally.

8.4. Conclusion

The purpose of this assessment was to create a general method, employing conventional techniques that are modified with sorbed gaseous state to accurately estimate the amount of adsorbed gas that sometimes represents half of the total gas in shale.

Even though, the range of the possible input values was substantial and the uncertainties in such assessments of shale gas resources are high, the obtained result seemed reasonable. Furthermore, the data for the resource calculation was reproduced by probability distributions as shown in the figure above (Figure 53), in case to validate the offset range. In contrast, other assessments, such as the ARI procedure, which do not have proper range balance, tend to evaluate the resource base with a median value, and thus slightly higher results. Implementation of optimal value range is the most reasonable comparison for the different results. A comparison table (Table 13) of the results from this calculation for Alum Shale with other assessments` outcomes, delivered by agencies, companies and independent research papers is provided:

Table 13 Comparison of results for shale gas potential in Alum Shale given from other agencies with this assessment

Comparison of different evaluation results for the shale gas potential in the Danish Alum Shale					
Resource base	**Issuing Agency**				
	ARI/EIA (2013)	Medlock Jaffe & Hartley (2012)	Kuuskraa et al. (2011)	USGS Gautier et al. (2013)	This Report (2014)
TRR or URR	32	23.5	23	6.9	**22,5**

This infers for high unrealistic values from EIA/ARI report of 2013 (32 TRR), with a large deviation from other sources shown, such as USGS (2013) with 6.9 TRR. This is probably due to inconsistency in methodological procedures, and different approaches in the reservoir and prospective calculation. The assessment derived from this study, situates between the ranges of the agencies depicted in the above table.

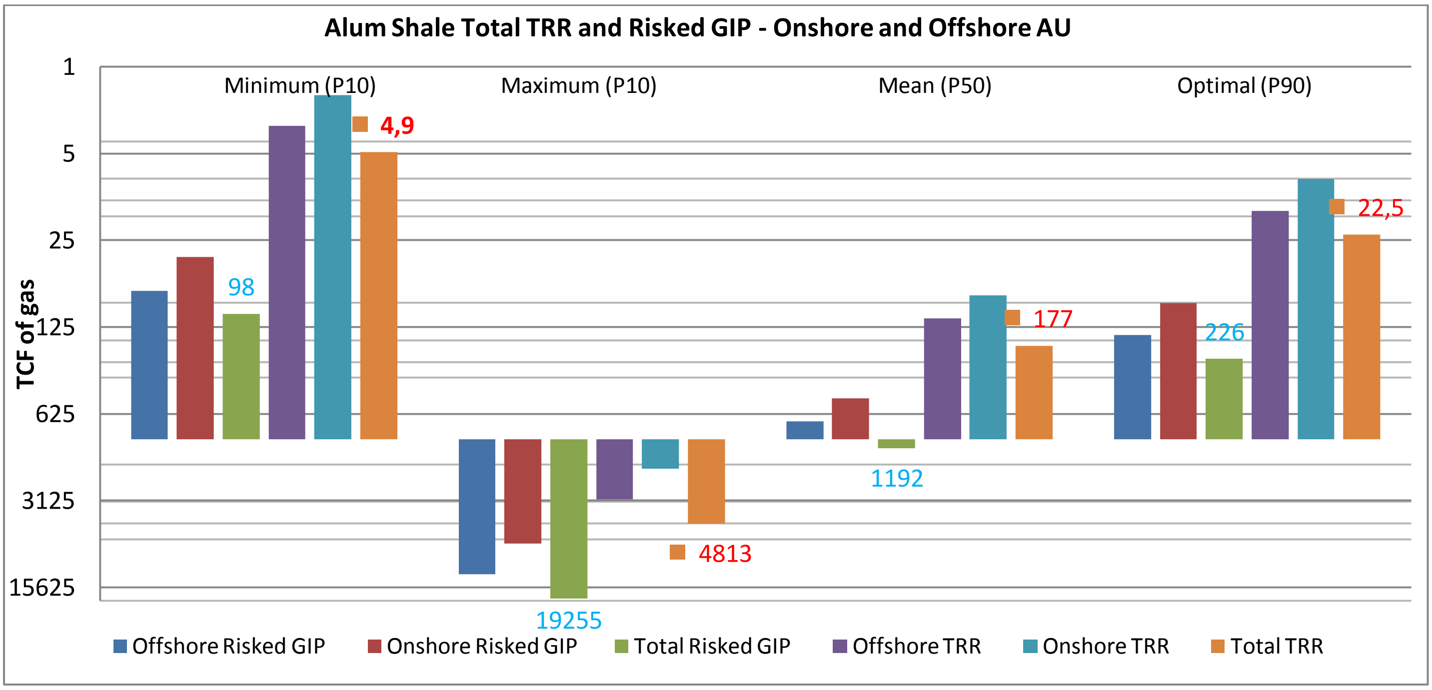
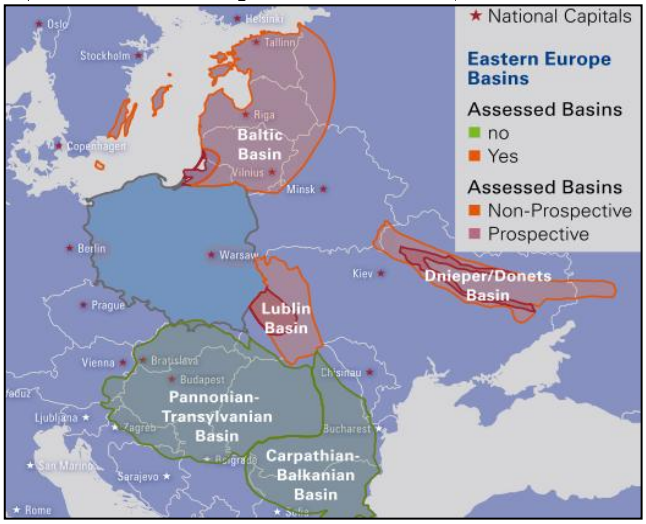


Figure 53 Graphical depiction of resource potential in Alum Shale for different probability ranges

9. Case Study: Bulgarian unconventional hydrocarbon resources with a focus on the Carboniferous strata

There are three distinct prospective basins for shale gas in Eastern Europe. The basins include the Carpathian Foreland Basin, the Dnieper-Donets Basin and the Balkanian Basin - Moesian Platform (Figure 54). In those basins mainly Silurian, Carboniferous and Jurassic sediment successions are targeted for shale gas exploration. In Bulgaria (Moesian Platform) only the Jurassic and Silurian have been thoroughly described, with no attention drawn on the Lower Carboniferous formation. Therefore, this study will try to examine the shale potential area and argue, whether there are any future prospects for commercial unconventional oil and gas extraction form the Lower Carboniferous strata (Konarska and Trigorska Formations).



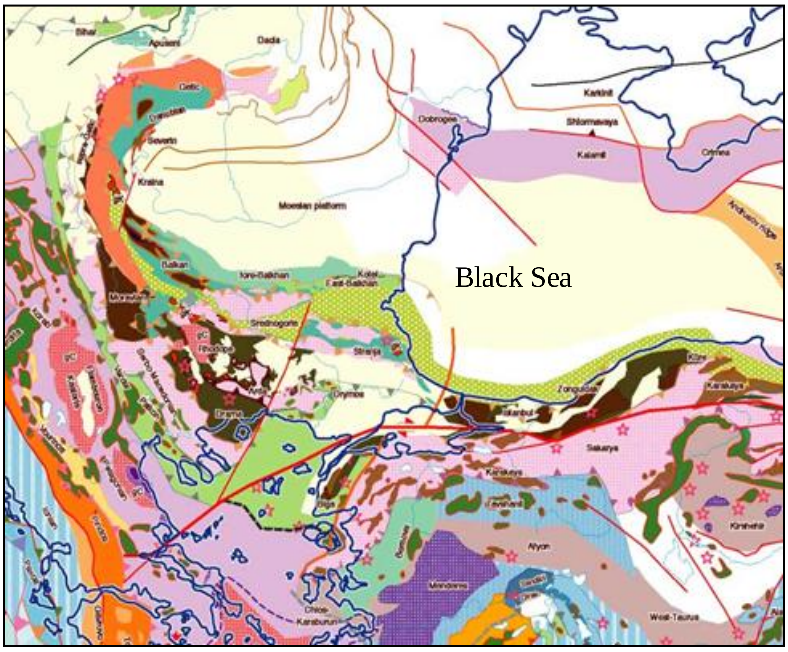


Figure 54 Delineation of prospective sedimentary basins for shale gas extraction in Eastern Europe (left) and a tectonic scheme of the South-East Europe depicting the location of the Moesian Platform in Bulgaria (ARI) (after Tari, 2010)

9.1. Potential hydrocarbon-generative successions in the Bulgarian part of the Moesian Platform

The Moesian Platform is a foreland basin which is situated between the overthrusted by the Balkan thrust system on the southern edge, and the Carpathian thrust system forming the north edge boundary, which events have Cenozoic age and are linked with Alpine tectonics (Alpidic thrustbelts) (Molatov, 1997). The platform is part of the European Plate, and a well known prolific and mature oil and gas province west from the Black Sea (Tari et al 1997) (Figure 54 right).The adjacent Getic Basin of Romania, which is the foreland basin of the South Carpathians, includes the same hydrocarbon source rocks prospective for oil and gas is less good because of deformation by Tertiary tectonic events (Kuuskraa, 2009). The deepest part of the basin in the western part of Bulgarian can reach 13 km. The basin includes carbonate-rich Paleozoic and Mesozoic rocks. The thick Paleozoic source rocks include Silurian black shales, the good-quality reservoirs of the fractured Devonian carbonates and Middle Permian to Triassic continental and shallow marine facies successions above the Hercynian unconformity, all result in favorable hydrocarbon generation and entrapment conditions (Tira et al., 1997). After the extension in the Paleozoic-Mesozoic boundary (aborted rift), a compressional regime in the platform was established (Norian-Rhaetian), which resulted in producing a north-vergent foreland thrust-fold, belt (Georgiev et al., 2001). The most important event for the conventional hydrocarbon generation, migration and accumulation was the Cimmerian unconformity formed in Lower Jurassic post-orogenic uplift and subaerial erosion of the belt (Georgiev, 1993) (Figure 55). A large carbonate succession form the Middle Jurassic to Lower Cretaceous was formed, due to a southward passive margin. The docking of the Balkanides took place in the Eocene, whereas the Carpathians stopped their collision in the Miocene, when the platform was finally shaped (Georgiev et al., 2001). The conventional reserves discovered in Bulgaria, are small in number, and are produced from the Triassic dolomites or basal Jurassic sandstones (Georgiev, 1996).

The thick Pz-Mz sedimentary cover of Norther Bulgaria has a long history in exploration of oil and gas conventional resources that dates since 1949 (Georgiev, 1996). Most of those medium petroleum pools nowadays are in their declining rates or depleted. It was confirmed by geochemical studies that, premises exist for commercial unconventional petroleum resources on the territory of Bulgaria (Velev, 2013). The Upper Carboniferous according to the geo-pressure ambiance, geothermal regime, catagenetic evolution and subsurface depth of the Mogilishte formation (Velev, 2013), is likely to be suitable for CBM extraction.

Unconventional hydrocarbon resources in Bulgaria exist in numerous geological intervals. The major intervals for shale gas development and extraction in the Bulgarian part of the Moesian platform are specified by LNG, Direct Petroleum, TransAtlantic Petroleum, Chevron, and the U.S. EIA`s assessment. All of the latter mention the Etropole Formation (Jurassic) in the western part of the foreland area of the platform, and the Lower Silurian succession in the NE part of the country (Figure56). Excluding shale gas potential sites, there are also tight gas and/or Coal Bed Methane (CBM) in the Upper Carboniferous (Mogilishte formation) positioned in the Dobrudzha Coal Basin, tight sandstone oil and gas reservoirs of Babinska and Mitrovska Formations (Ladinian-Carnian), and the Kostinska and Ozirovska Formations (Early Jurassic).

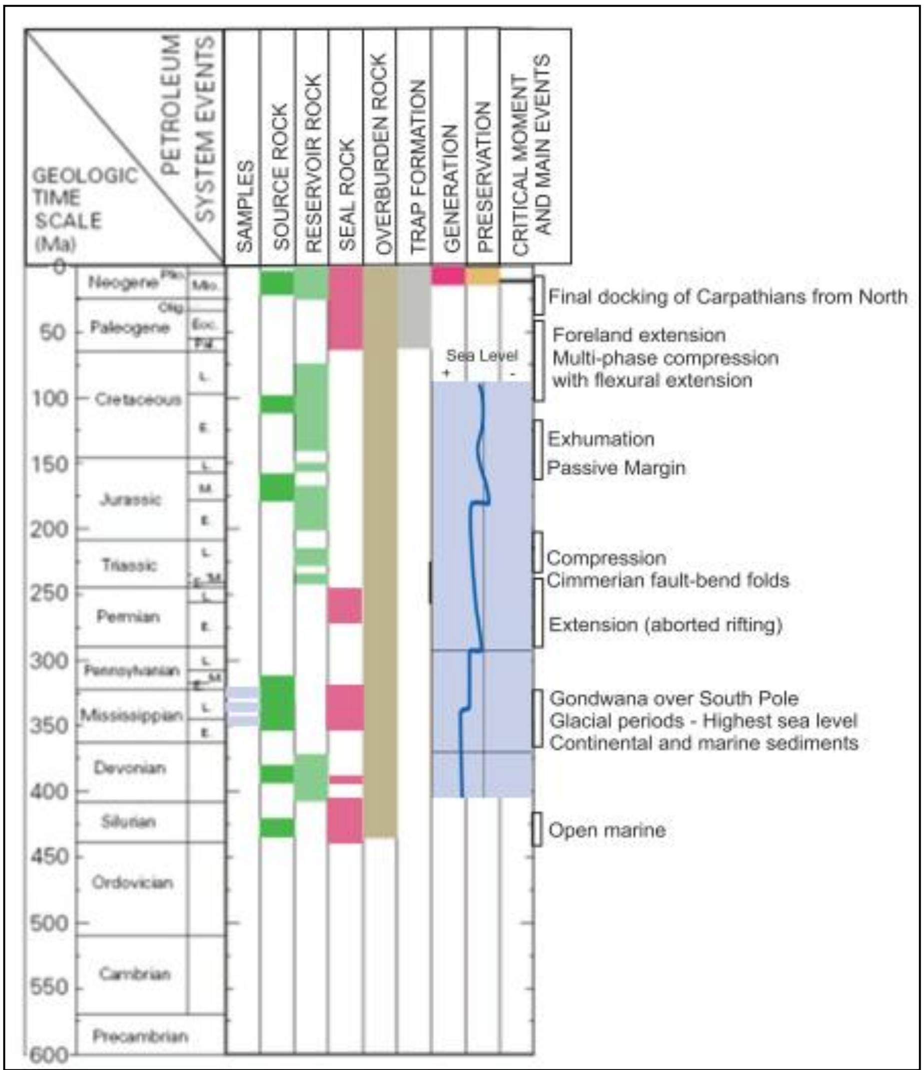


Figure 55 Chrono- stratigraphy and hydrocarbon-generation potential in the Bulgarian part of the Moesian Platform. The main source rock intervals are positioned in the Silurian, Early and Middle Jurassic, Oligocene and Upper Miocene (Sarmatian). The hydrocarbon formations from the Lower/Middle Jurassic shales are generative during the Middle-Upper Cretaceous period. In its north the platform has mainly a HC-generation period in the Late Neogene, due to rapid burial of Paleogen/Neogene source rocks (13 km deep sedimentary basin). In paleo-geographical terms, during the Lower Carboniferous, Gondwana moved over the South Pole and experienced several glacial-interglacial periods, which resulted in global sea level changes, where transgression and regression events were taking place on the low-lying craton margins. As the global sea level reached its maximum during the Mississippian Period (C_1) the carbonate Moesian Platform, was in partly marine exposed. (After Tira, 2010)

Several licenses have been granted to LNG (2011), Chevron (2011) and TransAtlantic Petroleum in the regions. Chevron seems to be attracted by the Lower Silurian black organic-rich shales, but until now they only researched the Vetrino-2 borehole (Figure 56), which has insufficient geological data, resulting in unfavorable for shale gas extraction ankimetamorphic grade of metamorphism (Velev, 2013). The company asserted that they can extract up to 8 TCF of technically recoverable shale gas from the country (Chevron, 2009). On the other hand, the Economy and Energy Minister has suggested that Bulgaria`s shale gas resource could range from 11 to 35TCF (EIA/ARI, 2013)[1]. Public opposition started to grow in the country after environmental organizers pledged for attention. The discussion, disclosure procedures and tension in regard to the social acceptance led to the execution of moratorium in the country in 2012, banning further activities. Shale exploration was put on hold along with the initial shale leasing. Today, high uncertainties are prevailing for any availability of shale gas resources, because no production testing has occurred. The main research activity in the country in regard to shale gas is the Shale Gas Research Group (SGRG) which represents a consortium of Sofia University and Bulgaria`s Institutes of Geology and Organic Chemistry, with the aim of long-term investigation of organic-rich shale formations in Bulgaria. Several license blocks have been identified as prospective in the country.

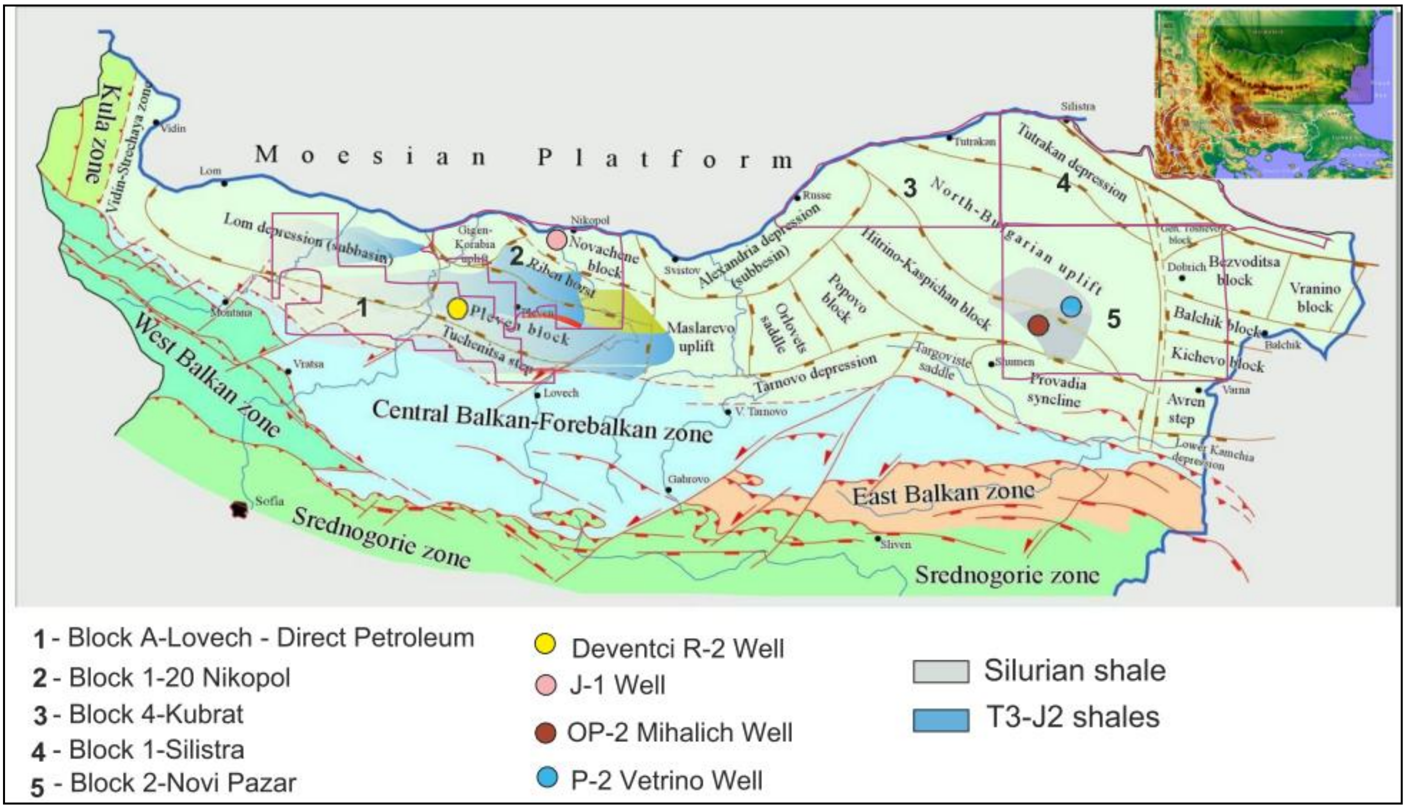


Figure 56 Delineated area of shale gas basins in the Silurian (grey) and Middle Jurassic (blue) formations in the Bulgarian part of the Moesian Platform. The numbers (1-5) represent license blocks granted to Chevron (5) and Direct Petroleum (1).The succession investigated in this thesis (Lower Carboniferous) is situated in Block Nikopol (2), with the depicted well J-1 (pink circle), from where the samples, relevant for this study derive (after Nikolov 2008).

9.1.1. Devonian-Silurian succession in NE Bulgaria

Novi-Pazar block (Figure 56) is viewed as the main focus of shale gas/oil exploration and future production along with the Silurian shales. It is mainly positioned in the Bulgarian Arch (Figure 56) in eastern Bulgaria (which coincides partly with Dobrudzha Coal Basin).Corroboration has been made that the prospective lithotype is the silty shale in the Devonian-Silurian strata with existing thickness of the Silurian organic-rich beds of 650 m and 2 km for the whole D-S interval in the depth interval of 800-2800 m. The geological data limitation in the region hinders managing prospects. Previously in the vicinity of the delineated area, there were several wells, but two of them are most important for the Lower Paleozoic succession – OP-2 Michalich P-2 Vetrino (Figure 56). Well OP-2 Michalich drills through Middle-Devonian dolomites, whose age is derived by conodonts (Spassov,1987, Boncheva,1995,2000).Even though the crystalline metamorphic fundament of the basin was not reached in those wells, they penetrated the whole Silurian interval (P-2 Vetrino borehole) stalling the wellbore in the Ordovician strata (3002 m, P-2 Vetrino). With the highly detrial block-faulted Lower Paleozoic strata in the North-Bulgarian Uplift and absent gas response in the cutting or during laboratory tests with gas chromatography, this interval is deemed as non-prospective with high risks of gas retention and deprived of future interest. Furthermore the negative signature of early chrono-stratigraphic occurrence of the generative potential of the Ordovician-Silurian black shale formation, which has ended in the late Paleozoic or in the beginning of the Mesozoic era, suggests absence of any oil- or gas-containing source rock (TOC< 1%). Adding the impact of late litogenetic transformation of the clay matrix (anchizonal), which does not possess any sorption capacity, and the highly coal-lithificated fossilized organic matter that yields only acidic non-hydrocarbon gases (CO_2 and H_2S), concludes the suspicious given potential for the Silurian strata by several companies.

Comparing the Silurian Shale in Bulgaria with the Polish and Romanian source parameters, it can be inferred that the TOC of the first is lower (less than 1%), with equal thermal maturity - in the gas window (mapped by conodonts alternation index – 1.3-3.5% Ro). The block of Novi Pazar has been estimated of having and area of 4,400 km^2 with 0.3 to 1.0 Tm^3 of gas reserves (EIA, ARI 2013). The exploration status in the latter will probably diminish in interest, because unfavorable source parameters (no hydrocarbon fluids, high depths, low TOC quantity) and complex geological conditions. Furthermore, any gas captivated in the Lower Paleozoic succession will have negligible quantities or will not be extractable.

9.1.2. Middle Jurassic prospective for shale gas in Etropole Formation

Etropole formation (Jurassic analogues of West Siberian producing formations – Bazhenovska and Igrimskaga (Upper Jurassic (J_3)) is given large potential with high expectations for shale gas/oil exploitation. This shale is considered having the main source rock potential in NW Bulgarian block of Lovech-Koynare with the drilled well of Deventci R-2 reaching the Lower Jurassic at average depths of 3800 m (Figure 56). The U.S. Energy Information Administration calculates the number of 148 TCF risked gas in place (GIP) and 37 TCF of recoverable reserves, with some 0.4 Bbbl of extractable oil resources in both the Bulgarian and Romanian part of the platform for the Middle Jurassic (EIA/ARI, 2013). However, as previously stated, it was confirmed that the numbers given by the agency are in the high-end of projections for unconventional reserves. The composite success factor (area and play risk) is set for only 18%, confirming the absent geological data for the reservoir. Separately, Bulgaria has been calculated to have 17 TCF of recoverable shale gas on its territory. Still those are only prognosis, without any published assessments yet. Some of the characteristics of this shale play were given in Chapter I, with the most important ones being the thermal maturity, indicating gas generation window levels (1-1.5% R_{ev}), highly overpressured reservoir, TOC of 1 - 4.6%, wet gas composition and average depth interval of 2500-8000 m. The lower Stefanetz Member contains thick organic-rich shales, with bulk mineral constituents exceeding 50% of carbonate quantity interbeded with marl and limestone. The marine depositional environment and the prevailing type II of kerogen, coincides with the screening criteria for shale gas/oil extraction (TransAtlantic Petroleum, 2012). Furthermore, the abnormal pressure gradient (0.78 psi/ft or 1.6 bar/10 m) confirms the good conditions for shale gas and oil production. Furthermore, Etropole fm. contains both oil-prone regions (north) and wet and dry gas ones (south) (Chevron, 2011). Similarities of the Etropole shale are found with its analog of the U.S. shales being the Haynesville Shale (Upper Jurassic) (EIA, 2013). The U.S. Energy Administration informs for production rates of 530,000 ft^3/d from the silty, sandy and carbonate intervals of the conventional well in Peshterne R-5. The fields of Dolni Lukovit and Dolni Dubnik (Jurassic) are correlated with the Etropole Shale (Georgiev 1993, 1996).

9.2. Lower Carboniferous hydrocarbon generation potential

In the Dnieper/Donets (Easter Ukraine) trough several oil and gas fields were established due to large hydrocarbon potential of the Lower Carboniferous Beds, which sourced most of the conventional findings. The best quality source rocks in the region are considered to be the Upper Visean Rudov strata (Stavlov, 2010). Similarly in the Carpathian-Balkan Basin, traces of hydrocarbon retention and hydrocarbon potential are established in Lower Carboniferous source rock successions. On the Bulgarian territory of the Moesian Platform several petroleum systems exist, where the major hydrocarbon generative potential in the Carboniferous strata lies in three main formations: Belgun, Trigorska and Konarska (Figure 57). The sediments are in argillaceous/siltstone facies, interbeded with coal seams with average thickness of 200-800 m. The retention of hydrocarbon fluids is thought as favorable, because of HC findings in deeper and younger Carboniferous formations, but still much needs to be interpreted for the proper structural and burial history of this period. The three distinct source rocks are characterized by different lithotypes and reservoir characteristics:

Konarska fm. (Kulaksuzov, Tenchev, 1973) is represented by polymictic metaclastic sandstones alternating with siltstones, shales and thin coal beds. The formation lies above Trigorska and is overlaid from Irecheska formation (Figure 57). The depth interval in which it has been encountered by well number 53 is 1186-1590 giving its gross thickness of 404 m, with the age of Upper Vise (Figure 57).

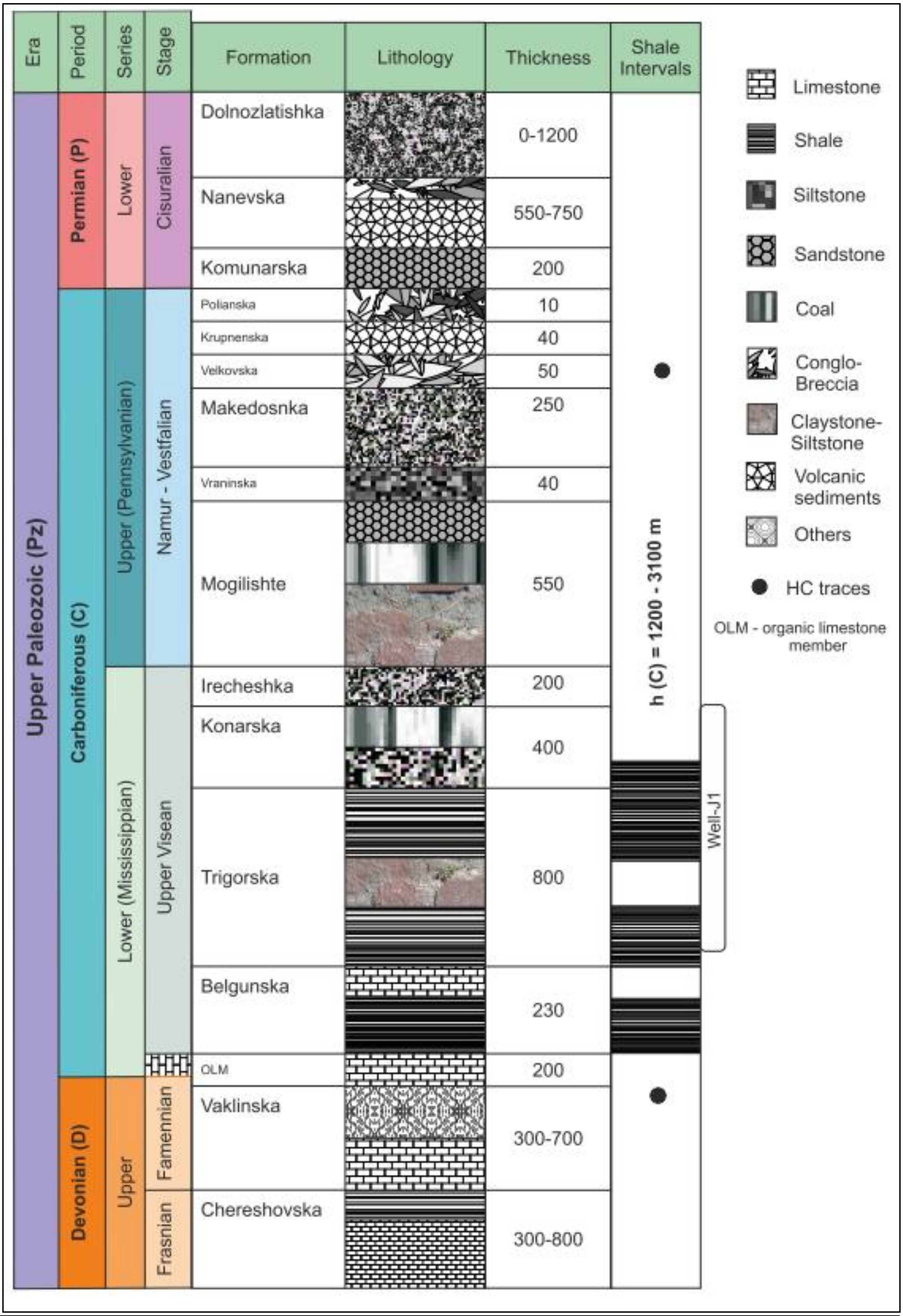


Figure 57 Litho-stratigraphic profile of Lower Carboniferous in Bulgaria and J1-well main investigation interval for this study (after Qnev, 1979)

Trigorska fm. (Kulaksuzov, Tenchev, 1973) comprises of deferent lithotypes including siltstones with less sandstones, shale, and rare distribution of thin-bedded limestone. The holotype section of the formation is set in well 53 (likewise Belgun fm.) in the interval between 1590-2634 m. Trigorska formation replaces laterally and downwards Belgun formation, whilst it upwards Konarska fm. The thickness is indexed as *1044 m*. Foraminifers assign the formation with Upper Visean age. Its areal distribution is mainly in the NNE part of the Moesian platform in the Dobrudzha Coal Basin.

Belgun formation (Kulaksuzov, Tenchev, 1973) is represented by mudstones and organic limestone with thin interbeded laminas of black argillites or sandstones. The full sedimentary profile of the formation has not been drilled, but only an interval of 226 m (2634 m – 2860 m) with intermittent core sampling in well number 53 in the vicinity of the village of Belgun. The formation upwards with erosive boundary the Chereshovska fm. and downwards by alternating in facies to Trigorska fm. (Figure 57) .The succession is determined with Middle-Upper Visean age (C_1) by foraminifers and conodonts, and is mainly found in the Dobrudzha Coal Basin (North-East Bulgaria). Other authors (Spasov & Gorak, 1985) confirm the lithotypes in the formation, and classify them as shale with thin sandstone intrebedding and redeposition of Devonian limestone in the base of the interval, and argillaceous and siltstone in its upper part.

In the Lower Carboniferous succession in North Bulgaria (Moesian Platform) recently well J-1 revealed and corroborated for some lithological characteristics previously concluded in the interval. The drilling data for well J-1 was provided along with depth maps, lithological profile and thickness of the shale intervals estimated by gamma ray logging. The well location is established in the geological structure of Novachene Block in North Bulgaria. The drilled Carboniferous strata in the well profile encompass the following potential shale sedimentary formations that were penetrated by the borehole (Figure 56 and 58):

Konarska fm. – in the depth interval of 2750-2950 m lithotypes shale, siltstones and sandstones were drilled (Figure 58). The siltstone/sandstones were grey to brown in color, with bulk mineralogical material composed of quartz, mica and 10-12% of carbonates ($CaCO_3$). The shales were dark-grey to black with low siltstone quantity. The grey sandstones are micro-granular and vertically fractured. Furthermore, coal laminas evaluated as bituminous were abundant in the succession. Main shale intervals are 2751-2818 and 2848-2923 (Figure 58).

Trigorska fm. – siltstones, dark-grey shales with minor interbeded sandstones were drilled. The argillites showed thin-bedding with 2% $CaCO_3$, no precise layering, and dense structure. Siltstones were described as grey, quartz abundant, with clay cemented. The sandstones in the interval posses also clay cementing. For the drilled interval in Trigorska fm., two lithotypes are determined in contrast of each other – upper mainly argillaceous/shale part (2950-3910 m) and lower terrigenous/clastic part (3910-5160 m) (Figure 58). The main intervals with shale/mudstones for future potential yield of hydrocarbons are:

- In the Upper part – from **3100-3700** and **3735-3910** m, wherein the interval of 2950-3100 m, the proportion of clay and clastic sediments equalizes (50:50) (Figure 58).
- Lower part – **4600-4680** and **4780-4820** m. (Figure 58)

In each of the two prospective predominantly shale formations drilled (Konarska and Trigorska), **2/3** of the total thickness was evaluated to be considered as the major and crucial thickness criteria, when evaluating the shale gas/oil potential and in-situ resources. As the whole thickness in J-1 well of the Lower Carboniferous interval accounts for 2200m, this infers to **1400 m** of mean/average net thickness of both formations (Figure 58).

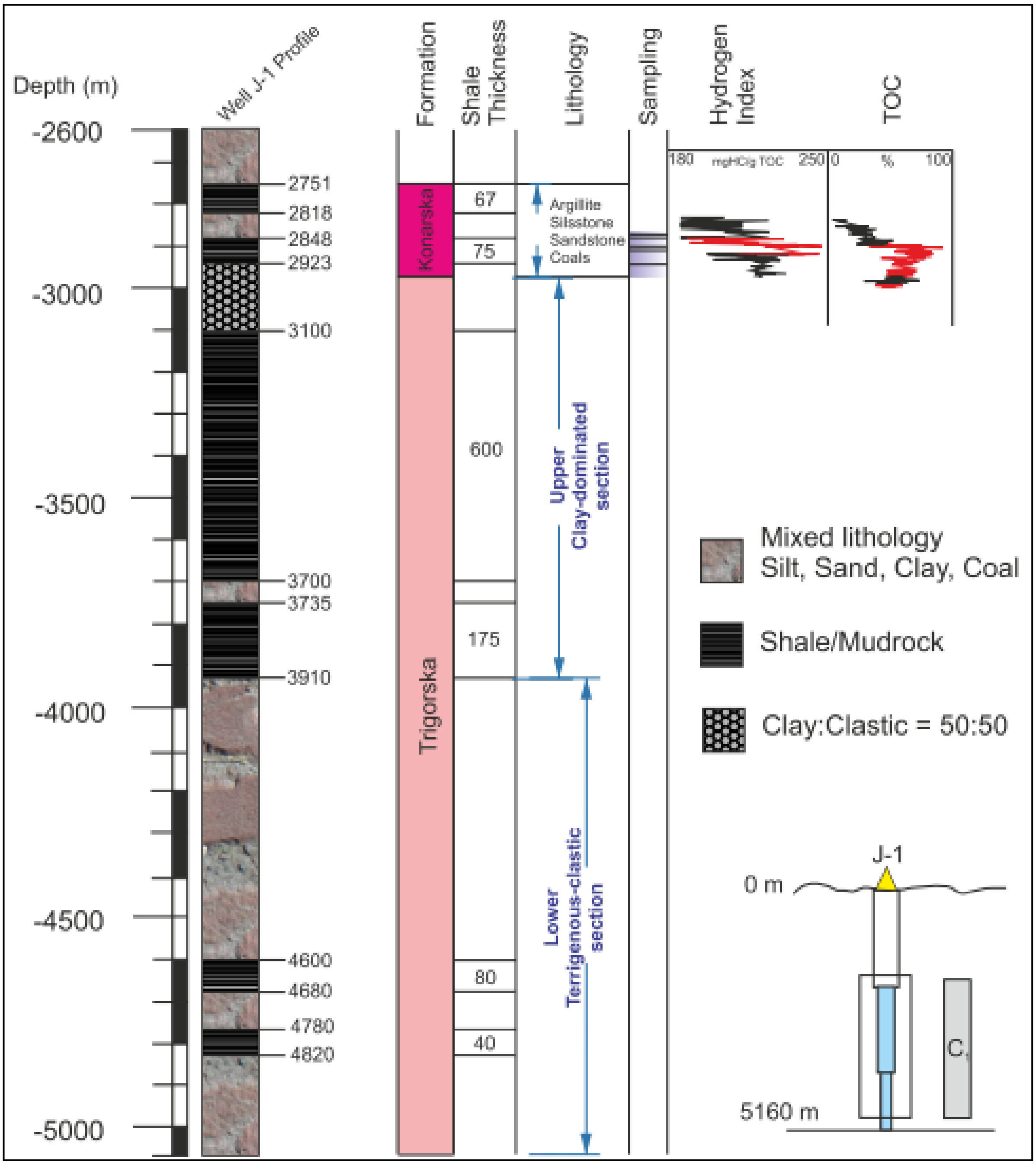


Figure 58 Litho-Stratigraphically cross section of borehole J-1 in the Lower Carboniferous strata (Konarska and Trigorska Fm.)

The thickness of the Lower Carboniferous succession can vary greatly in the NNE Bulgarian part of the Moesian Platform. It is mainly focused in two different localities. The area in the central northern part of Bulgaria is deemed the thickest, with values in the range of 500- 2500 m (Figure 59). The J-1 borehole area thus coincides with the datum for the highest thicknesses (more than 2.5 km) observed from the isopach map (not to be mistaken with isochore, which measures vertical thickness and not real stratigraphic perpendicular to the bedding thickness like the isopach map) . The whole depth that J-1 drilled was very unusual and unexpected for the Lower Carboniferous succession on the territory of the Bulgarian part of the Moesian Platform. Furthermore, as the polygon schematic map shows (Figure 59) the tendency towards south of J-1 well is that the whole Lower Carboniferous interval <u>is thinning in a short distance</u> <u>and is even absent in southward direction</u>. The thinning of the isopachs has erosive and truncation character, whilst their thickening is due to structural dissimilarities (Figure 59). The both prospective source rocks (Konarska and Trigorska Formations) are distributed within the Dobrudzha Coal Basin delineated area. They lie beneath the base of thick coal Upper Carboniferous interval. Above Konarska Formation the younger Irecheska and then the Upper Carboniferous thinner Mogilishte Formation are positioned. The thickness of Mogilishte formation is several grades lower – 500-600 m, than the Lower Carboniferous succession. The Lower Carboniferous interval has moderate to high areal extent with calculated number from several figures to 4500 km^2 (Figure 59), and maximum thickness of 3100m (Qnev, 1978, 1994). For comparison Mogilishte Formation in the Namurian part of Upper Carboniferous has a spatial distribution of only 100 km^2. Some 30% of this area should be subtracted, because of insufficient thickness, depressurizing risk of reservoir rocks due to uplift and erosion in previous geological periods, along with unfavorable reservoir parameters or immature level in the rest of the partial non-sweet spots, leaving nearly 3300 km^2. The optimal depth interval for the Lower Carboniferous inputted in any statistical models or evaluation assessments should be between 1500 and 5000 m, with conservative average shale net-pay zone thickness of 750 m west from the fault and south from the Danube (2/3 from average 1500 m). The second locality of thick Lower Carboniferous strata is positioned in the Vranino Block of the furthermost part of North-East Bulgaria (Figure 59) should not be deprived of attention and is included in the area having low-end thickness criteria with the assumption that areas above 500 m of total thickness are deemed as prospective (sweet spots), due to the larger coal amount in the area. The top in the J-1 well is encountered

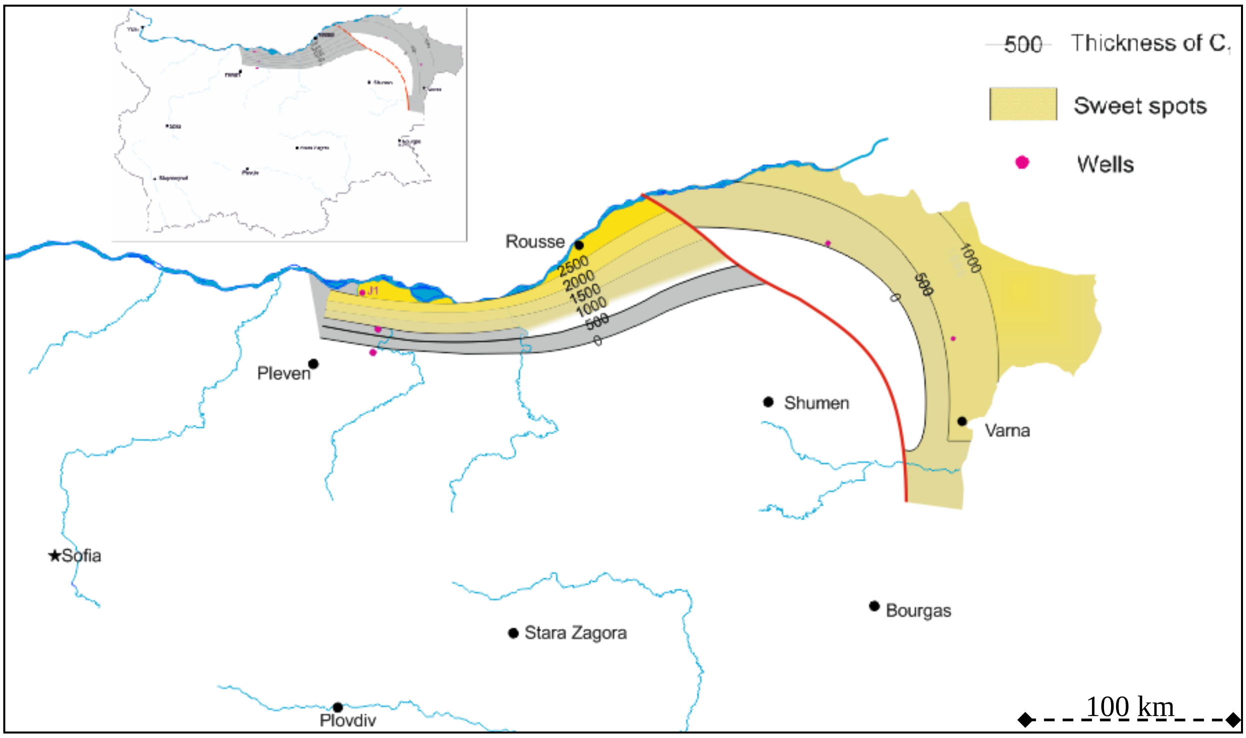


Figure 59 Isopach map of distribution and thickness of Lower Carboniferous sediments in NE Bulgaria (after G.Georgiev 2014)

In order for the Lower Carboniferous succession to have moderate or high hydrocarbon yield potential, it is believed that the thickness of the latter should not be less than 1000 m in the area west from the fault (south from the city of Rousse on the map), in case the main source rocks – Konarska and Trigorska Formations experience deep burial and generation or retention of their oil or/and gas potential.

9.3. Laboratory session results from the sampling of well J-1

The extracted sample from well J1, were provided for analyzing the hydrocarbon-generative potential for certain Lower Carboniferous formations. The four samples obtained, include mudrocks, siltstone, shale, argillite and coal lithotypes. The full inventory and physical properties of the samples can be found in Appendix C, along with the measurements and experiments executed for each one of the debris. The canister "containing principle" for the shale samples was strictly applied in order for retaining light-hydrocarbon components (exhalation of methane), with no or negligible curing-transportation period applied.

Only results from the laboratory work relevant for the petroleum properties, geological and depositional factors affecting the rocks, and the pore-type systems developed is addressed here. Main experimental sections for the samples were the RockEval analysis, Dual-SEM photo-micrographing, moisture content, gas chromatography and the polarized optical petrographic analysis conducted after treating one of the samples with epoxy into a polished thin-section (Table 3 Chapter I).

No X-Ray Diffraction (XRD) analysis was carried through the study, which is why the main mineralogic characteristics were obtained by the photomicrograph. The common composition of sample BG1.1-J1 can be seen in the depiction and table below (Figure 60). The other shale sample also showed the same ratio of constituents, while the coal samples (BG2-3-4-J1) were not examined under a petrographic microscope, but have been judged only by macro-scaling, which inferred vitrinite maceral composition.

Parameter	Common characteristics of sample BG1.1-J1 (%)
Quartz + Feldspar	27 - 30 %
Clay content	32 - 40 %
Vitrinite	6 - 9 %
Carbonate	9 - 13 %
Kerogen	7 - 9 %
Moisture content	1 - 2 %
Total Organic C	11 %
Others	2-5%

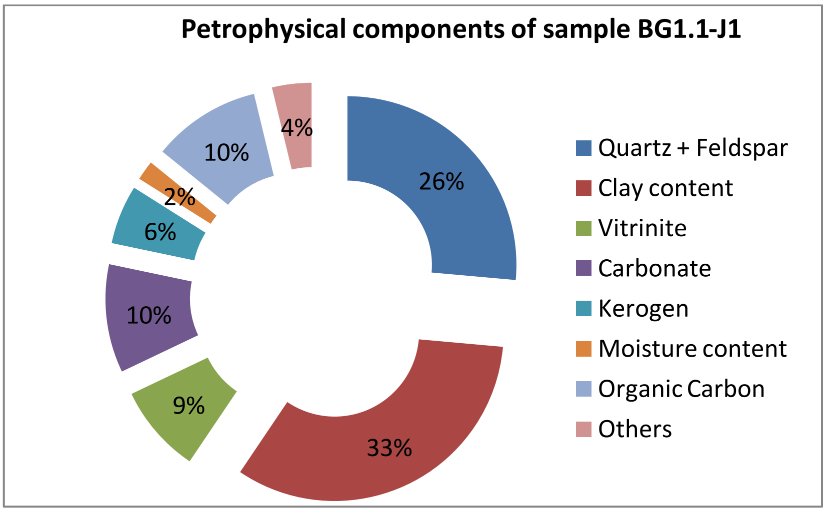


Figure 60 Petrophysical analysis results with bulk mineral constituents and fluid or hydrocarbon phases for Konarska Formation (Lower Carboniferous)

9.3.1. Petrographic and photo-micrographic analysis

The thin section provided detailed description of the texture, framework of grains, pore system and authigenic minerals identifications in the mudrocks-siltstones-sandstones-limestones and other sediment lithotypes. The analysis was conducted with the preliminary basis that the gas-generation potential of Lower Carboniferous in Northern Bulgaria will be in close relationship with the petrophysical parameters of the different lithological parts of the reservoir, which are capable of retaining the generated hydrocarbons. Even though, no conventional oil has been obtained from this specific source rocks as a precursor, still the unconventional gas character of those should not be disregarded.

Pore inter-accessibility was investigated for sample BG1.1-J1 derived from petrographic images (Figure 60) of polished impregnated thin-section. Interconnectivity of pores in the sample showed good patterns in different particle sizes. The organic matter is thought to be pyro-bitumen (Figure 61 (b)), with relative abundance of 9-12%, inferring from the microscopic analysis. On some images (Figure 61 (b)) it can be seen the change in the surface texture of the OM, which is mainly found in macro-fractures and mesopores. The matrix structure is in the micrometer scale, mainly consisting of bulk detritus components ((d) and (f)). Recrystalise quartz crystals, mica, silt, sand and clay are mixed in a non-proportional ratio, with silt and clay having the biggest percentage in the targeted intervals of J1-well (2751-2818 m and 2848-2923 m) (40-60%). The quartz crystals (c), governing for long sediment transport (and deposition) are most likely to be detrial extra-basinal with low effective properties in cementing the shale/siltstone bulk minerals. Usually quartz is cemented by silica from smectite-clay ilitization during diagenesis according to the reaction: (Boles and Franks, 1979)

$$\underline{\text{Smectite} + K^+ = \text{Illite} + \text{Silica} + H_2O}$$

As in the case of the shale sample BG1.1-J1, low values of quartz and elevated content of clay can diminish the brittleness to a certain degree. The mudstone petrographic image represents thin beds of clay-rich and silt-rich lithology (Figure 61 (a) and (d)). Furthermore, the vertical and horizontal heterogenicy viewed during the analysis showed to exceed the one found in other typical shales or sandstones. As discussed before, the volume of kerogen, deposited syngenetically with the minerals, is expected to be more than its weight percentage measurement (wt %).

The almost 40% of the volume in Konarska formation (sample BG1.1-J1 and BG1-J1) was calculated to have alumo-silicate (clay group) origin, which is non-homogeneous, altering pattern`s sediment beds with inclusions of sandstones and siltstones. They are the main carriers of organic matter, with highly laminated texture (Figure 61). This led to the assumption that the sample belongs to the newly identified "Hybrid Gas Shales" resources (Speight, 2014).

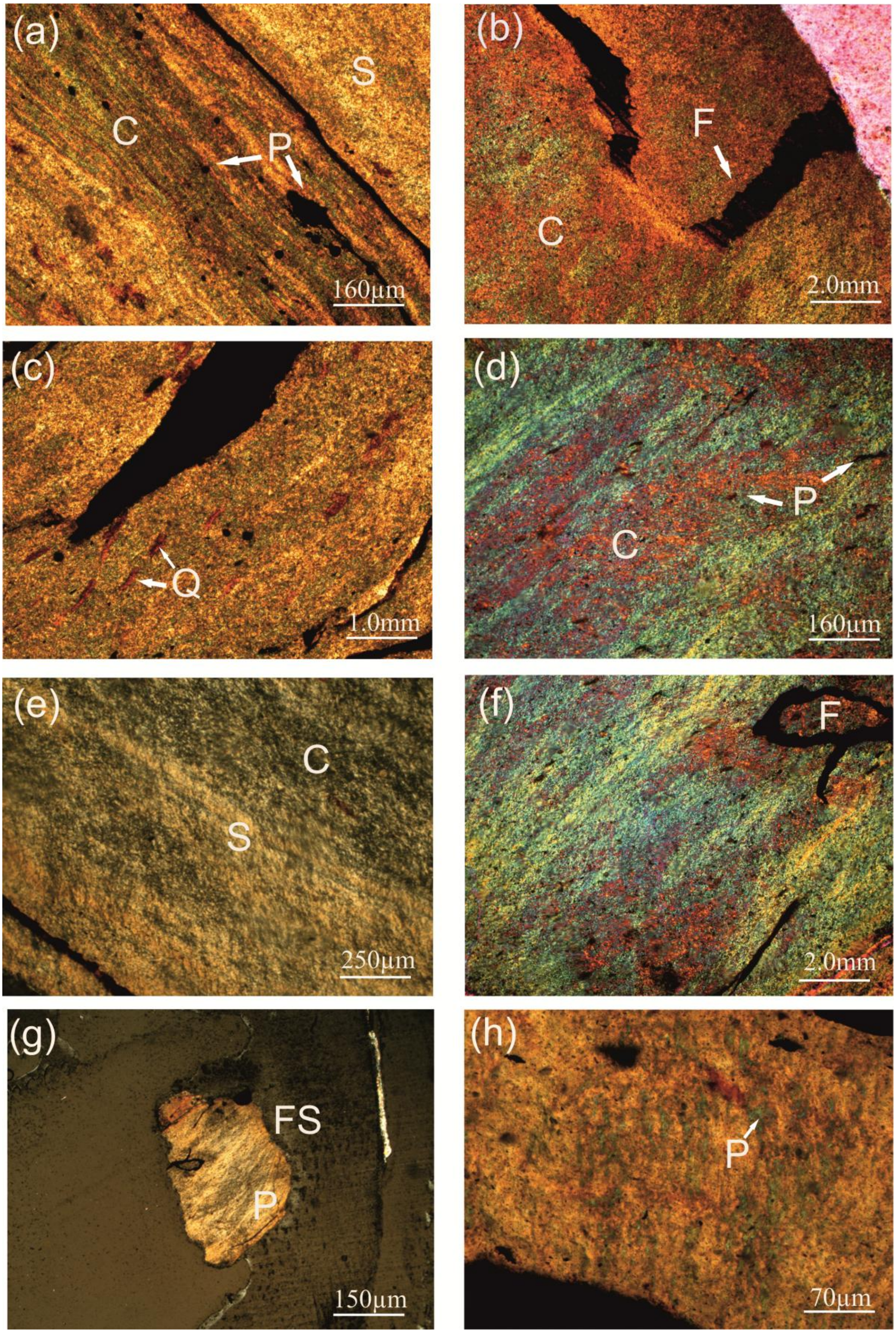


Figure 61 Optical polarized petrographic analysis and photomicrograph of shale/siltstone sample BG1.1-J1 (Tmax = 434-438 oC with HI 191-212 Depth of 2847 m) across the North Bulgarian area, which derived from impregnated thin section, showing detailed bedding and composition variations on the sub-centimeter scale. (a) Depicts thin kerogen layering in macro-fracture pores with volume percentage of 9-12% along with parallel altering layers of silt and clay sections. (b) Intragranular texture layering on organic matter, corresponding to several stages of pyro-bitumen "cooking". (c) Planar macro-fractures with elongated quartz crystals disseminated in the matrix inclusion adjacent to the organic matter. (d) Meso- and micropores filled with OM. Surface porosity was calculated to be 3.5% (black fragments). (e) Different silt/sand (light) and clay/argillaceous layers (dark). (f) Ubiquitous micro-pores in both clastic and argillaceous layers. (g) Feldspar crystal representing rock fragment moldic pore with residual dissolved grain – intragranular pores may exist. (h) High sigma (lateral) stress secondary re-opened pores in the matrix of the shale. Q-quartz; FS-feldspar; P-pore; F-fracture; C-clay; S-silt/sand;

In their basics, such potential unconventional resources comprise of high sand-silt components among the shale layers, which act favorably in enhancing the permeability. Furthermore, the foreign minerals result in low stress gradients and higher brittleness, which ranks shales with such lithotypes included, even better for production due to high recovery rates (40-45%) (Speight et al, 2014).

The various litho-mineralogical detritus and the scattered in the micro-millimeter pore space kerogen are concluded to have a terrestrial deposition pattern, within a lacustrine or deltaic environment. The organic matter, which is a potential source of hydrocarbons, is present in all the lithotypes in different forms, judging from the images – clastic, detrito-fragmented and disperse. Even though, the shale does not meet the force-attribute of having a marine origin, still it is deemed to be main source rock in the Lower Carboniferous (C_1) of the southern part of the Moesian Platform (North Bulgaria). The low calcite quantity (10-12%) of sandstones and siltstones with expected high clay minerals (40-60%), infers for favorable geo-mechanical properties for shattering the rock by exceeding the formation (fracturing) pressure, due presence of $CaCO_3$ and other silicates. However, ductility of non-marine shales is mainly a consequence of elastic modulus and stress properties of clay minerals (illite) as discussed in Chapter I. This can further infer that these hybrid shales (ductile and brittle) with compression stress and lateral strain can both be present with fluctuations depending on the ratio of minerals in different sections. Deeper intervals of well J1 (3100-3700 and 3735-3900 m), where no sampling was established, well logs, confirm that the proportion of the clastic material equalizes with the clay minerals (50:50) (Figure 58). Furthermore, unlikely for the formation, some volcanic ash and components were detected during the pleochroism testing of the matrix and the photo-micrograph. One explanation is that the material has been re-deposited in the sedimentary depots (lakes, lagoons), where it encountered much higher acidic environment resulting in its geochemical transformation to clay minerals. Therefore, the reservoir rock investigated expelled petroleum products during the pyrolysis analysis in slow and hard manner.

As shale is composed from mineral components of mud primarily, the composition of the reservoir can vary, due to the tiny grains of clay and quartz, and so can the porosity, permeability and the capillary entry pressure. Pore volume compressibility governs the pore size along with the deposited fluids and their flow paths. All those petrophysical characteristics of the shale or siltstone rock provide the confounding nature and complex determination of this type of sediments during lithification and the later evaluation of their OM entrapment or the decomposition and reburial methods. The numerous and micro-scale minerals in the shale matrix and cement constitute for long sediment transport and low-tidal deposition province.

9.3.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy technique provided high magnification/high resolution images of the smallest features in the shale samples (nano-pores). The apparatus can investigate authigenic clays and cements associated with pore systems of unconventional reservoir rocks. The analysis was done in a low-pressure chamber using gold-coated samples or another alloy (gold/palladium). It identified the micro- and nano-pore systems in the mudstone/siltstone pulverized debris, by backscattered electron beam. Argon-ion milling has to be used in preparing the surface of samples for the analysis, which provides a polished section suitable for backscattered imaging (by reducing the effect of charging of uncoated samples).

The analysis was performed with the optional aim for identifying the major pore-types present (inter- and intra-pores) and their size-scale ratio. The BG1-J1 and BG2-J1 samples are composed overall of 20 to 50% quartz, 30-40% clay minerals and some small quantity of carbonates. Sample BG1-J1 (5.6% TOC) was found to have abundance of vitrinite maceral in its pore structures, whereas sample BG2-J1 (TOC of 78%) is considered to be coal-lithificated sediment with a shale/siltstone precursor. The enriched alumo-silicate pelitic-sized component of the rocks found from the petrographic analysis, and the introduced images below ((a) to (f)), can constitute for high sorption capacity of the Konarska formation. The volcanic sediments found during the PetroAnalysis maybe the reason for the lowering of the filtration parameters of the porous lithotypes – siltstones or sandstones. The dissolution pores (image (e) below) and the coal cleavage layering (f) in the clastic localities of the sample, are corroborating the moderate to high amounts of gaseous hydrocarbons that could be retained in the interpores` space. The laboratory SEM findings enlightened the main gaseous phase in coals and shales and defined it as methane, with no occurrence of bituminous oil-prone components in liquid or solid state. The gas is found not only in the shale or coal matrix but in macro-fractures.

The highly fractures soft minerals (clays) suggest an overpressure reservoir with high elastic stresses exerted during faulting and structural events. Gas adhesion (adsorbed gas) is situated mainly in the mineral surfaces (clays), where the sizes of the crystals can vary between 1 micron and 1 mm. The low relief of the silt and clay minerals suggests high dehydration state. Furthermore, a secondary porosity system in the dissolute part of the crystals is expected to be present or in the organic matter.

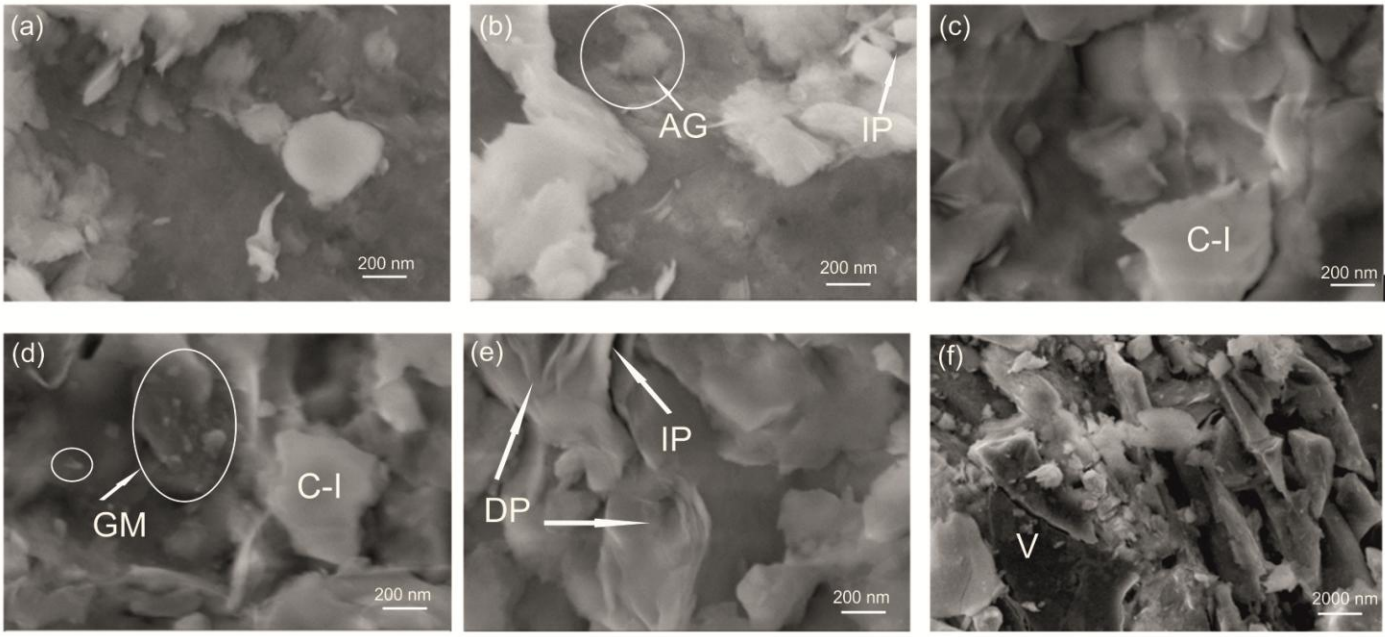


Figure 62 SEM images of sample BG1.1-J1, BG1-J1 and BG2-J1. (a)adhesive reactive plate mineral grains; (b) nano-scale gas adsorbed gas molecules on the micritic matrix (c) clay (illite) irregular crystal shape; (d) nano-scale intragranular pore above the illite crystal, and the adjacent free gas molecules; (e) dispersive and laminated dissolution (intraparticle) pores in the nano-scale section, along with elongated intergranular pore (600 nm); (f) microscale vitrinite crystals in the coal-rich sections of the shale/siltstone sample; AG – adsorbed gas; GM – gas molecules; C-I – Clay – Illite; DP – Dissolution Pore; IP – Intergranular pore; V- vitrinite crystals.

Because the rock showed premature levels of thermal maturity from the RockEval analysis, the volume of the organic matter is expected to be less than 25%, with very low distribution of kerogen in the secondary pore system. This infers that for this formation the organic matter porosity (OM-pores) will not have a significant meaning for the shale-gas storage patterns. Image (c) shows a free gas fraction in the macro-pores system (1000 nm) surrounded by the plate-like crystals of illite, whereas the intra-pores in image (e) does not indicate any hosting of gas phase. This is why, as a conclusion it is obvious that almost the whole quantity of gas present in the samples, was in free state with less being in solution or sorbed. The presence of free gas is mainly linked with the macro-fracture system and bulk meso-pores.

9.3.3. Moisture content analysis

Moisture quantity in shale reservoirs can reduce significantly the storage capacity for hydrocarbon liquids. The dehydration of clay minerals is intense during the diagenesis stage where the moisture reduction in the reactive minerals tends is observed. However, in the C_1 shale reservoir, moisture quantity can be affected by the overpressure state of the reservoir, and thus retaining the pore water phase due to high capillary pressures. This leads to intense saturation of water in the matrix system, and exhalation or replacement of hydrocarbons previously occupying the void space. Moreover, moisture effect on sorption capacity of dry gas (CH_4) in in-situ reservoir conditions cannot be fully examined in laboratory environment (Gasparik, 2013). High temperatures exerted in high depth intervals with different geological setup, result in a complex and dynamic system that should be treated carefully. The clastic lithotypes in Konarska formation have the specific property of clay concentration patterns (illite), which result in almost 40% of the bulk mineralogic matrix composition.

The carried experiment for the moisture content, included a simple pre-weighting of the sample in initial state, followed by drying to a certain degree, and a post-measurement of the weight loss due to vaporization of water. This led to a 1.05% (with a tolerance of 0.1) water contained initially in the shale/siltstone sample (BG1-J1). A 0.5 g of the starting weight was diminished to 0.487 g in the first run of the experiment. This percentage of 1% moisture content cannot make a significant change and alter the hydrocarbon saturation on pore and matrix level, thus for this reservoir, the water content of the mineral phase is less important qualitative parameter.

9.3.4. Gas Chromatography analysis

Samples BG1-J1 and BG1.1-J1 were both inserted into a GC with a helium carrier gas continuously flowing from a cylinder through the injection port, the column and the thermal conductivity detector (TCD). A sophisticated apparatus was used, where the pulverized sample was in solid phase, when preheated to 125°C. After extraction of the volatile phase by a syringe, it was carried by the inert gas (non-chemical interaction), to the packed capillary column (13 m long) which was coated with thin film (0.2 micron) of high boiling liquid (i.e. stationary phase). The detector then quantitively represents the volatile phase in a peak representation (electrical signals).

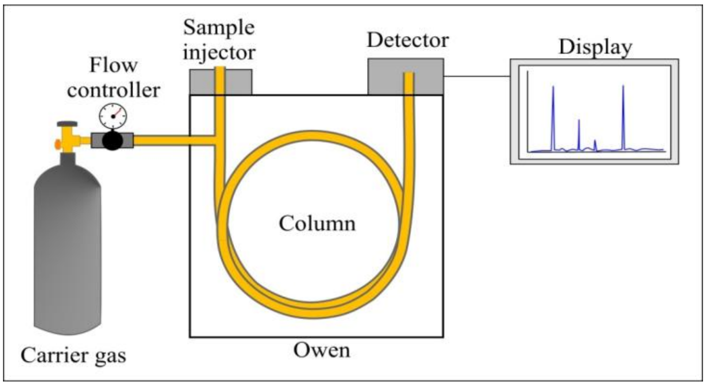


Figure 63 Schematic representation of a typical gas chromatograph`s setup (Naturwissenschaften, D. Der. (2013))

Before the measurement, due to the biogenic gas calibration of the chromatograph, the outcomes of the integrated peak area differed between the two samples (Figure 64 and 65). Only parent molecules in the gas content retrieved from the samples were viewed, inferring for simple alkane composition (light paraffins), i.e. methane (CH_4), in both samples (Figure 64 and 65).

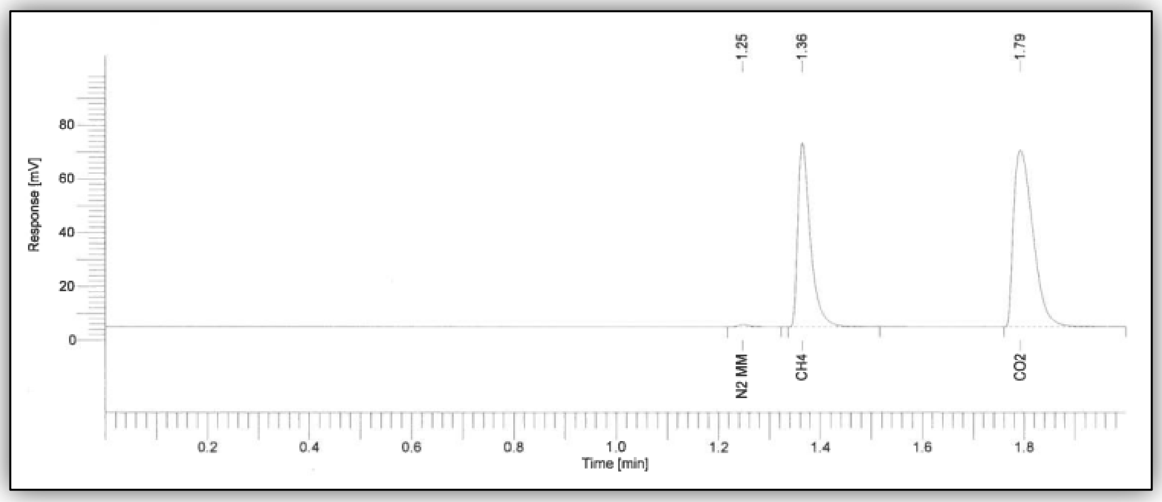


Figure 64 Response peaks from GC measurement for sample BG1.1-J1 (TOC = 11%). Note that the CH4 peak is having almost ideal peak-shape, while the non-organic presence of the CO2 response infers for broader peak with some disturbances.

Additionally, no other saturated alkanes were noted, but only inorganic gases comprising of high amount of CO_2 and nitrogen (trace-gas). The reason for the detection of only CH_4 constituents is maybe of several reasons. First of all, the entire detector (thermal conductivity) that uses helium may sometimes miscalculate the sensitivity of the analysis. Even though, using a TCD brings quick analytical results, it does not provide the same outcome as the one using flame ionization detection (with a carrier gas being nitrogen). Secondly, sometimes not the whole sample is in gaseous state, but may be mixed with liquids or other gases, which pose problems. During the experiment, the high pre-heating temperature was sufficiently monitored so that the whole composition was converted to gas, and exhaled from the solid phase. Finally, the results can deviate in couple of magnitudes, depending on the proper retention time and peak curvature, meaning that solute molecules are acting independently.

The experiment was repeated several times, so that the perfect peak shape (ideal) can be obtained. The broad, fronting and asymmetrical shape of the peaks in sample BG1-J1 for the methane and carbon dioxide may express undesirable interactions that take place during the chromatographic analysis. This is usually a result of slow kinetics of mass transfer in the packed columns (Rate Theory).

The second sample (BG1.1-J1- Figure 64 up) showed almost an ideal peak for the methane response with 1.36 min. of retention. Calculations for the peak height were done, in order to evaluate the exact gas percentage and methane quantity in the second sample having area (A) of 118806 [uV*sec], and height of 68410 [uV], which in total sets a **50.38 %** CH_4 of the total volatile phase exhaled BG1.1-J1. The quantity of CO_2 similarly fluctuates between 27-32 %. Such portions of CO_2 are unusual, even though the existence of coal-bed seams in the formation is found. The unlikely presence of huge amounts of CO_2 is related with the high carbon exhaled from the cleavage and cleats` systems of coal interbeded in the formation. Still a tolerance of 3-5% with an offset in measurement could be possible.

Sample number BG1-J1, responded with almost negligible amount of CH_4 and final adjusted amount of **3.5% (**Figure 65). Further laboratory results and identification procedures for the chromatography can be seen in Appendix D.

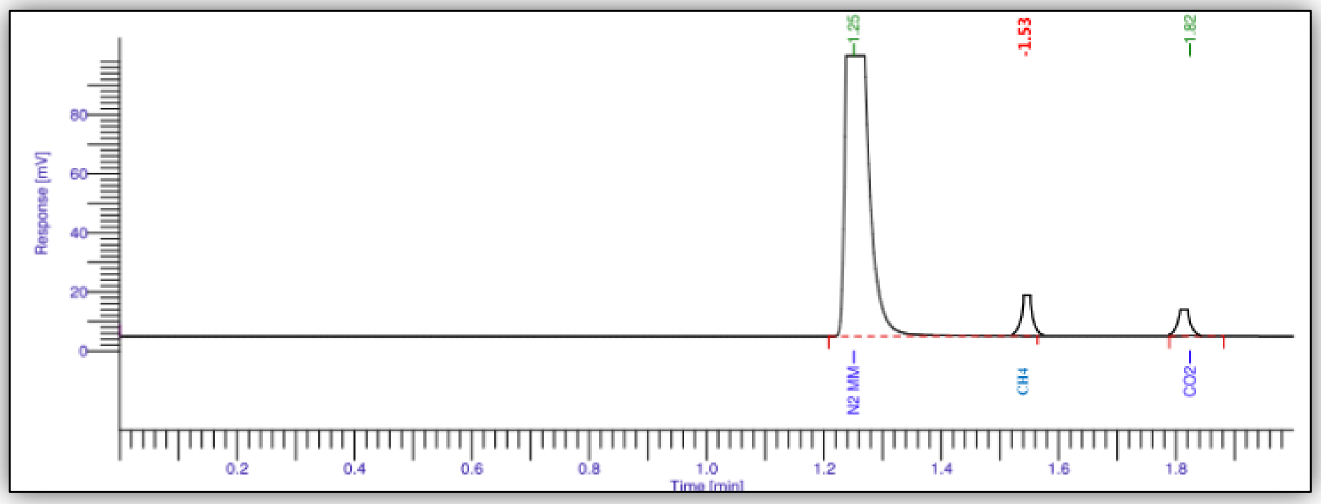


Figure 65 GC response for sample BG1-J1 treated with nitrogen and helium carrier gas. All of the peaks show asymmetrical to fronting tendencies. Quantity of dry gas (CH4) is in the vicinity of 3%.

The high surface area in the packed column with the adsorbent provided maximum interaction of the gas with the immobile liquid, and thus if there were any heavier alkanes in the system, they would have been detected. However, the methane origin cannot be confirmed without precise biomarker identification. Knowing that the samples represent the shale/siltstone sets of the Lower Carboniferous in North Bulgaria with current depth of nearly 2900 m, such dry gas, should be treated as an oil precursor (thermogenic), rather than biogenic gas. Nevertheless, a correlation to a secondary migration of the CH_4 and CO_2 from syngenetically deposited coal beds in the basin might be possible. Another theory may be authigenic development of the CH_4 and CO_2 gas from the kerogen in the formation or the introducing of the phase from the interbeded coal laminas. There was no evidence of gas before in the near formations of the C_1 succession, except of the Upper Devonian (Famennian) Vaklinska fm. which is sealed by the organogenic limestone member (OLM), and has shown traces of light oil in fractures (Well C-9 Kardam, depth 908 m).

9.3.5. RockEval pyrolysis analysis for all five J-1 well samples

The biggest concentration of the organic matter is situated in the coal layers of Konarska formation. They have been examined for the moisture content (1.25%), with a subsequent analysis of the ash content, which resulted in identification of low- to high-ash coal seams. The petrologists have marked the coals from the profile of Konarska formation (sample BG2-J1 and BG1.1-J1) to "gas-generating" with vitrinite reflectance altering from 0.75 to 1.87% R and ranking them as high volatile bituminous (VB) to medium VB (Hristov et al. 1988). The latter, examined the Upper Carboniferous Mogilishte Formation to have significant hydrocarbon potential – 25cm^3/g of mass in the raw coal matter (daf) (Hristov et al. 1988). If this theoretical notion is true, a similar numbers should be expected in the even deeper C_1 Konarska and Trigorska formations (2800-5000 m). The organic matter in samples BG1-J1 and BG1.1-J1 showed high TOC quantities (Table 14) with low hydrogen index (212), inferring for kerogen type II/III, consisting of humic-type organic precursors. This indicates that the generating capabilities of the OM and respectively Konarska fm. are to yield mainly gas hydrocarbons. As former studies concluded (Hristov et al. 1988), that the coefficient of coal yielding is in the vicinity of 6%, and the result from this report of dry gas signature for Konarska formation viewed in the chromatograph measurement (CH_4 = ~50%), there is enrichment and minor hydrocarbon potentials in the examined strata.

Low mature oil generation stage (primarily) is thought to be the result of either soluble organic substance at premature stage or biodegradation at the initial stage after the oil generation threshold (VRo = 0.5-0.7%) is accessed by the kerogen. This type of premature oil is developed before the peak oil generation and it results in biodegradation of kerogen. An option is the gas present in the shale/siltstone reservoir to have a biogenic precursor.

The typical parameters obtained from the pyro-analysis (RockEval II) are depicted in table below (Table 14). The main potential focus in the interpretation stage concerns mainly the two mudrocks/siltstone samples (BG1.1-J1 and BG1-J1).

Table 14 Pyro-chromatographical characteristics of shale/siltstone and coal samples from Konarska Formation (C1)

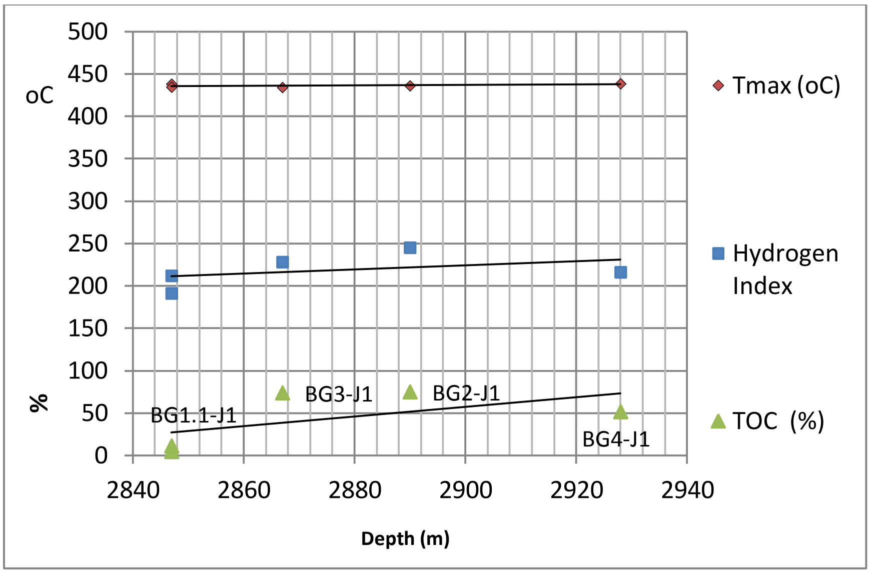
Sample Number	Depth (m)	Lithology	S_1 (mg/g rock)	S_2 (mg/g rock)	OPI S_1/S_1+S_2	TOC (%)	Tmax (^oC)	HI, S_2/TOC	Kerogen type	Maturation level
BG 1-J1	2847	Shale/Siltstone	0.18	8.7	0.02	4.5	438	191	III	Immature
BG 1.1-J1	2847	Argillite/Silt	0.51	23.2	0.02	11	434	212	II/III	Immature
BG 2-J1	2890	Coal	6.46	183.4	0.03	75	436	245	II/III	Pre-mature
BG 3-J1	2867	Coal	5.77	168.3	0.03	74	434	228	II/III	Immature
BG 4-J1	2928	Shale/Coal	4.28	111.3	0.04	52	438	216	II/III	Pre-mature

Comment: The measurement along with the parameters` determination were derived in the laboratories of GEUS (Copenhagen)

First of all, the considered clay-rich intervals in the Lower Carboniferous succession of the Moesian Platform were encountered across the drilled area of well J-1 at depths between 2751-2818 and 2848-2923 m within the Konarska fm. The samples from those intervals have shown sufficient enrichment of organic carbon with TOC of 4.5 to 11%. Considering that, typically the values for continental originating claystones/mudstones are between 0.9 - 1.5 % with a maximum of 3-4%, thus the TOC evaluated is extremely high for non-marine deposited argillites. A contributing factor, for the abnormal high TOC values, is the alternating lithotypes in the strata encompassing coal-beds, siltstones and minor portion of clastic material. The change of the facies, along the lacustrine to restricted-marine depositional environment lithotypes, corroborate for higher TOC values than the clark of the continental lithosphere`s ones. The sub-bituminous to bituminous previously ranked coals, show a TOC in the formation between 52 and 75 wt%, being a sub-lithological type in Konarska formation with low quantitive percentage.

At some depths (2950-3100) the fractured, polymictic sandstones have the same quantity as the clay component. They are thought to be low contributor for the carbon richness in the formation. Furthermore, the high TOC of sample BG4-J1 is interpreted to be a local incident-high value for presence of bituminous shales (2928 m). This depth interval is the lower part of the Konarska Formation, drilled in J-1 well.

The vitrinite in the coals was determined after a photo-micrograph analysis as micro litho-typical consisting of mainly internite maceral. This infers that, the coals should have influenced the hydrocarbon generative potential in the entity as total share of organic carbon. Values of HI suggest that some oil phase should be also generated or present, due to mixed type kerogen (II/III) , but such was not seen on the chromatographic measurement or observed in the petro-analysis. The range of retained hydrocarbons in the samples (S_1 peak) is from 0.18 to 6.46 mg/g rock. A similar dispersion pattern is seen in the late potential values (S_2 peak) of 10-180 mg/g rock (Table 15).



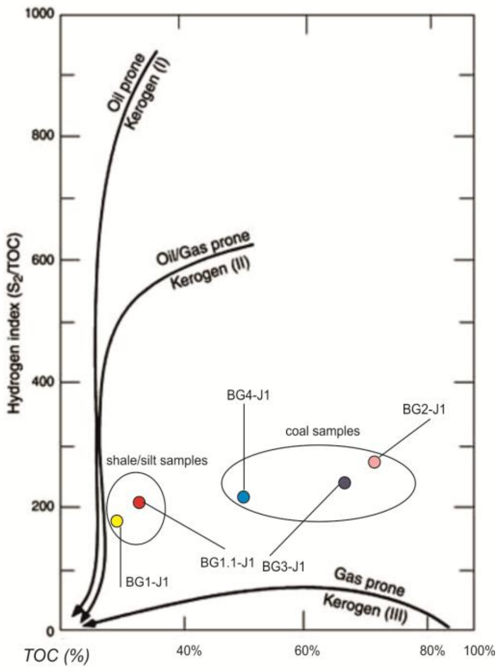


Table 15 RockEval analysis derived values of the pyrolysis for all four samples from borehole J-1 in North Bulgaria (left) and generative amounts of HC in the hydrogen index and kerogen type of samples (right). Note the pre-mature T-max trend (~430oC) and the low HI (~200) with high TOC for the coal samples (BG2-3-4 J1) of 70%, and for BG1.1-J1 of 11%. All samples have type II/III kerogen (right).

In case to justify the pyrolysis analysis, a vitrinite measurement should had been performed, so that the thermal maturity is compared with the highest exerted burial temperatures` history in the sedimentary basin, along with identifying the formation position in the hydrocarbon generation window – 60 to 120^{o}C (oil or gas). Besides in coal, vitrinite was abundant in the shale/siltstone samples, found in the sedimentary kerogen (OM). The shiny appearance (vitreous) can be instantly seen in a macro-scale view. The cellulose-lignin composition of vitrinite formed from the woody tissue of plants corresponds to terrestrial environments and type of OM (kerogen III), that yields mainly gas, with lacustrine or other deposition. Thus why, it is believed that the kerogen of samples BG1-J1 and BG1.1-J1 was derived from the same biogenic precursor as in coals (humic peat). The rich shale/siltstone intervals of Konarska Formation were probably saturated with vitrinite during the diagenesis. The abundant OM in the shales (TOC=11%), along with the non-marine origin and clastic content are the typical rocks for vitrinite to occur, after coals. Supposedly, the terrigenous lithological intervals (lower Trigorska formation) will have very low vitrinite content, or almost lack of organic enrichment. Abundant vitrinite macerals with high terrestrial input in the studied samples calls for a future measurement of the reflectance parameter of the maceral (VR_o).

The difference seen from the project`s executed RockEval data analysis and the theoretical notion of the interbeded coal in Konarska formation, caused a dispute point further to be investigated. First of all, the consistent data from the pyrolysis (judging from Tmax, S_1 and S_2 agreement) showed a rigorous argument for absence of petroleum generation in some degree. The pre-mature to immature level of the samples, compared with the formation temperatures (around 57^{o}C reservoir temperature if considered a gradient of 23^{o}C/km) constitutes for full overlapping of the results. This illustrates that the RockEval measurement is considered with no tolerance or offset difference in the technical and laboratory execution of the samples. Ruling out a failure of the apparatus, thus is considered improper. To resolve the inconsistency, usually vitrinite reflectance measurement would have been a promising argument. This however, was not performed in the scope of this study. The absent of sufficient well-data or maturity maps of the region, led to the confirmation of the empirical data at this stage. The discrepancy can be further discussed if a VR_o do exist form the same area of the J-1 borehole, as for now weight will be given to the pyrolysis showings. From a fundamental point of view, three reasons can cause such deviation of the RockEval readings and the formerly noted coal rank:

- The abnormal geothermal gradient (27-32^{o}C/km) experienced in some regions of the South-European plate can cause high maturity levels in shallow depths (formation temperature on 3000 m will be around 100^{o}C), and confirm or corroborate for the previous coal ranking in the Lower Carboniferous interval.
- Thermodynamically speaking, systems with instantaneous change exert duration periods of adjustment, which is described as Le Chatelier`s principle. The returning to the initial state is dependent on the strength of the negative feedback shock (Tomas, 1975). In the petroleum fluids` behavior, if a source rock formation is

overpressured (more than 0.478 psi/ft or 1 bar/10 m), it may experience retardation in its maturation development. Thus, the system counteracts, which requires time and adjustment, resulting in lower maturation levels. As the Konarska Formation is thought, as in this case not a normal pressured system, this may be one of the reasons for the showings of the RockEval analysis. Of course, significant change should not be expected form a normal to an overpressure reservoir, but only in the rank of the same stage of maturation.

- And finally, improper handling, transportation, canister sealing, and protocol for sampling research in the laboratory, may consequently develop misleading data from the measurements.

However, a firm evidence from the territory of Bulgaria are the anthracite (fat coals) derived from the Dobrudzha coal basin and present in the Lower Carboniferous source rocks. The interval level of 2890 m in the J-1 well area, was defined as in the same rank of maturation (300 Ma of the Visean sediments). The burial depths and the anthracite stage, is very well in agreement with the burial depths in the region.

9.4. Hydrocarbon potential in the Lower Carboniferous

The potential for unconventional oil and gas extraction and exploration in Bulgaria, including shale gas, tight oil and CBM, is narrowed to four specific “plays” or geological intervals. The Lower Carboniferous has yet not been included in such assessments of prospectus or neither has it been considered to have large hydrocarbons-generation potential. A comparison is introduced for the experimental outcome of this study with other main black shale formations targeted for unconventional exploration in the country (Table 16).

Table 16 Comparison between different unconventional hydrocarbon prospective formations in the Moesian Platform with included the Lower Carboniferous Konarska Formation from this study

Attributes	Prospective shale formation (polygon)			
	C_1 (Konarska, Trigorska fm)	C_2 (Dobrudzha Mogilishte fm.)	J_2 (Etropole fm. Stefanetz member)	Silurian (Vetrino Novi Pazar Block)
Thickness (m)	Gross-2000 (Net 700)	0-600 (Area-120 km^2)	7-185	over 1500
TOC (%)	5-11 % (mean 7.5%)	-	0.34-1.60	0.50-5.30
Vitrinite R_o%	0.8 – 1.88 (expected)	0.9 – 1.5	0.78-1.56	-
OM type	III	III	I+II	II (probably)
H-C shows	Free gas (CH_4) GC analysis	-	Free gas	-
Depth (m)	1000-3000 (mean)	1200-1800	2700-4300	1300 and more
Lithology	Claystones, siltstones, sandstones, coal, argillites	Sandstones, coal mudstones, siltstones	Argillites, siltstones	Claystones, siltstones, marls
Depositional environment	Lacustrine, shallow marine	Lacustrine, shallow marine	Marine restricted (anoxic)	Open marine
Type of play	Shale gas or CBM	Tight gas and CBM	Gas and oil shale	Shale gas

9.4.1. Single-well partial and theoretical assessment for Lower Carboniferous hydrocarbon potential

The data analysis of the depth map, thickness of the dominant shale intervals in Konarska and Trigorska Formation, the pyro-chromatographic findings, and the macro-scale porosity determination, led to incremental calculation of the resource-in place (GIP) for the core area of Lower Carboniferous strata. Insufficient data, such as adsorbed gas properties in the shale formation, accurate thermal maturity measurement, stress and permeability values impose highly uncertain results from the outcome of this evaluation.

However, the stratigraphic and geological parameters from the J1 well have enlightened some new information for the C_1 shale/siltstone rocks. The reservoir parameters for initializing the methodological approach of per-well calculation are:

Table 17 Input parameters and variables in the reservoir engineering calculation of per-well in-place resource estimation

Parameter	Mean Value
1.Porosity (Dimensionless fraction)	3.5
2.Volume Formation Gas Factor Bg (z, P, T)	0.0045
3.Gas saturation (Sg)	50%
4.Water Saturation (Sw)	50%
5.Depth (m/ft)	3000 m / 9842 ft
6.Thickness(h)	700 m / 2100 ft
7.Total Organic Carbon (TOC)	7.5 %
8.Sorbed gas capacity	20 scf/ton (?)
9.Sweet Spot Area	1235 mi^2/ 3200 km^2 / 790737 acres
10. Composite success factor (Play and Area)	18%
11. Estimated Ultimate Recovery (EUR)	No Data

The procedure form the case study for Denmark will be followed, only at certain grade, without applying values for EUR and sweet spot depth median per-well drainage area. By converting the area to acres and multiplying it with the 43,560 factor for the acre/foot result, and using the net thickness of the formation the value for the prospective area per acre will be obtained. The following engineering equation is applied:

$$\mathrm{GIP} = \frac{\mathrm{V_b(p)(1-S_w)}}{\mathrm{B_g(p)}} = \frac{2.8.10^{12}*0.5}{0.0045} = 311.10^{12} scf = 468\ Bcf/mi^2$$

- GIP – Free Gas In Place per acre/foot
- V_b – 43,560 x A x h x ϕ = bulk reservoir volume in ft^3
- 43,560 - ft^3 per acre-foot conversion factor
- A – Area, acres
- h – Thickness, ft
- ϕ (p) – porosity at formation (reservoir) pressure (p), fraction
- S_W – water saturation, fraction
- $(1-S_W)$ – Gas saturation (S_g), fraction
- B_G – Gas FVF at reservoir p, ft^3/SCF
- p – Formation Pressure , psia

This calculation corresponds to the quantity of only free gas in the Lower Carboniferous, with no accounting for any adsorbed gas still. Because no laboratory evidence exist on the Langmuir sorption isotherm, with the hypothetical adsorbed gas quantity, a value for G_C = **30 scf/ton** as an analogue is assumed with bulk density of 2.45 g/cm^3.

$$\mathrm{V_{ad}}(G_c) = \frac{V_{LCH_4} P}{P + P_{LCH_4}} \quad \textbf{and} \quad \mathrm{GIIP\ (ad)} = \mathbf{A} * \mathbf{h} * \rho * G_c \quad \textbf{or} \quad \mathrm{GIIP(ad)} = \mathbf{V_b} * \rho * G_c$$

In which, the G_C is the gas content (volume of gas/weight of shale) given by the Langmuir equation (left) with V_L (Langmuir volume at infinite pressure) and P_L (Langmuir pressure with 50% of the gas at infinite P has been desorbed), and the A – area, h – thickness and ρ – density of the shale formation.

$$\mathrm{GIIP(ad)} = \mathbf{V_b} * \rho * G_c = 2.8.10^{12} * 2.45 * 30 = 321\ Bcf/mi^2$$

$$\mathrm{GIP_{total}} = \mathrm{GIP_{free}} + \mathrm{GIP_{sorbed}} = 321.10^9 + 468.10^9 = 789\ Bcf/mi^2$$

After evaluation the gas content (798 BCF), the prospective area of 1235 mi^2 yields the following:

$$\text{Risked GIP} = 789.10^9 * 1235 * 50\% = 584\ Tcf\ and\ \ TRR = 584.10^{12} * 10\% = \mathbf{58\ Tcf}$$

The quick screening calculation and incrementally non-backed up with scientific data parameters for the sorption potential of the methane composition, showed a recoverable total in-place gas estimate in the shale reservoirs of the Lower Carboniferous - of 58 TCF for the whole delineated area of 1235 mi^2. This is based on sampling data from the middle-upper member of the Lower Carboniferous strata- Konarska Formation, and cannot predict the change in heterogenicy of the hybrid reservoir in regard to pore space, fluid saturation, permeability and geological complexity. The technically recoverable resources were obtained by first risking the GIP with a composite risk success factor (50%), and then a recovery efficiency factor (10%), which usually for typical shale formation in the U.S. (Barnett) is no more than 20-25%,. The result does not account for any mixed composition (CO_2) of the volatile phase.

9.5. Conclusion

The assessment presented in the literature by EIA (10.06.2013) on the Moesian Platform`s potential, in particular the Silurian and Etropole fm., encounter some dissimilarities with the opinion in the country (i.e. Velev 2013, Shale Gas Research Group, 2012). The assessment meets the 2% of TOC criteria for shale gas incorporated by the experts of the subcontractor Advanced Resources International (ARI). The authenticity of the used analytical data can be argued, and moreover the simplified sediment successions as a homogenous bodies. Numerous specific activities should be executed in the Moesian Platform, in case for the potential resources to be converted to production flows of unconventional fuels. Force ranking and delineating of parameters with a consensus upon the low-end of the TOC for all formations should be stated deliberately.

A single borehole in the Lower Carboniferous strata of the Bulgarian part of the Moesian Platform, cannot predict the heterogenicy in vertical and lateral directions throughout the whole succession and formation. From the litho-stratigraphic cross-section for well J-1 shows the abrupt and sudden alternation of different lithology in thin intervals, thus larger scale of parameter prediction will require denser well exploration procedure. Critical values for the formation, such as permeability, adsorbed gas properties, delineation and spatial area of the assessment unit in the Lower Carboniferous are with low- to moderate quality of assumption in the report to this point, which infers for incapability of forecasting any precise resource in-place, but only a value in the vicinity of the maximum range (**58 TCF**). Hopefully, as exploration is improved and geological data is acquired, exact reservoir and engineering values can be obtained for further investigation.

Table 18 Force-ranking attributes for the Lower Carboniferous source rocks succession in Bulgaria researched in this study for shale gas potential (Trigorska and Konarska Formations)

Force-ranking Attribute	Lower Carboniferous unit (C_1) Konarska and Trigorska Formations Assessed Parameters
1. Total Organic Carbon > 2 wt%	Yes (6-11%)
2. Organic Matter Type – I or II	No (III mainly – non-marine)
3. Thermal Maturity > 1.1%R_o to 3.5%	No (Immature (S_1,S_2,T_{max}))
4. Net thickness > 20 meters	Yes (Gross – 600 m, Net – 140 m)
5. Overpressured reservoir	Yes – Highly overpressured
6. Brittle lithology	Yes – Hybrid shale (silt, sand, coal, carbonate)
7. Geological history favors gas retention	No
8. Areal delineation and AUs	No (not defined)
9. Porosity > 4%	No (3-3.5%)
10. Permeability > 100 nanoDarcy	Yes/No (No core sample available)
11. TRR resource	**58 TCF (low probability value)**

Geologically after examining the deposition environment through the grain matrix in the petrographic study, it was concluded that the province of the sedimentary depot for the Lower Carboniferous succession in Bulgaria is similar to the basic model of coastal barrier sandstones grading to grey lagoon shales with brackish water faunas within a final packing of marginal swamp areas on which vegetation was established (Figure 66). This explains the mixed and mainly lacustrine/terrestrial organic matter type in the samples from Konarska Fm. Moreover, the processed (reworked) sandstone grains, plane-bedding sheets layout of shales, and the upward coarsening of the organic-rich shales and siltstones by thin discontinuous coals, draw a typical analogue succession as in the figure below (Figure 66). Back-barrier environments can also include tidal channels and flood-tidal deltas, based on exposures in the Moesian Platform (Horne et al.1979). The paragenetically formed coal beds with siltstone and sandstone lithotypes and the large thickness of the Bulgarian Lower Carboniferous interval (Konarska and Trigorska fm.), forms an interest in exploration and research in the area for both conventional and unconventional petroleum resources. However, even if some exploration commences, promising results are not expected due to the pre-mature signature of the RockEval measurement of Konarska Formation in the Lower Carboniferous strata.

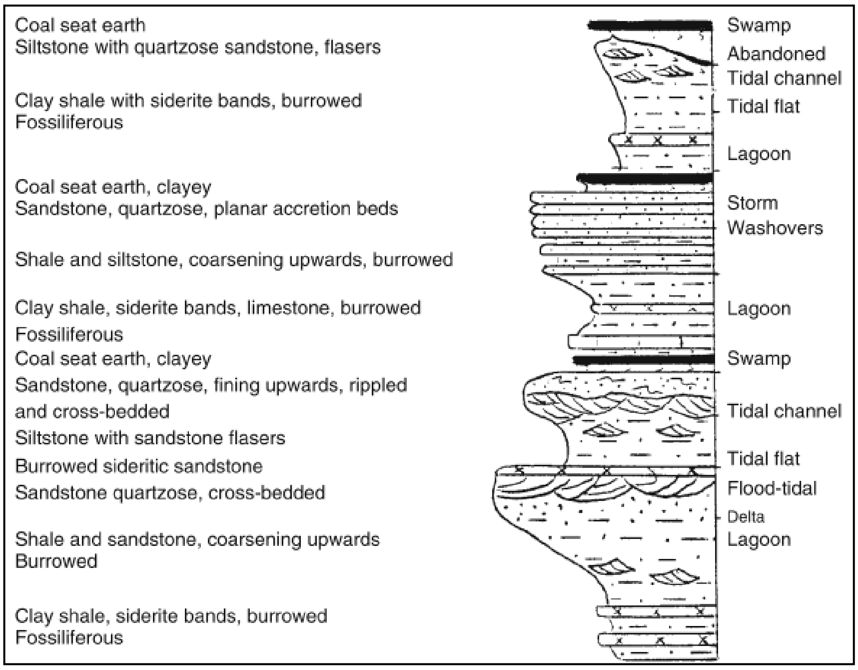


Figure 66 Barrier and back-barrier environments including tidal channels and flood-tidal deltas (Horne et al. 1979)

In order for unconventional petroleum resources to be explored and produced in Bulgaria several activities and acceptance procedures should be done in future terms. Special section for unconventional development or institution should be imposed in the competence of the government, with the aim of clarifying the problem and technology for unconventional completion methods, along with the activity for obtaining capital in the new industry. A robust consensus should be performed between the society and the industry, in order both sides to accept and apply the terms for production of such resources. Moreover, a thorough, precise goal-orientated and strategic research activity for evaluating the potential of unconventional and their in-situ resource should be executed. And finally, more reliable geological information should be obtained for the targeted formations, along with optimizing the measurements or reshape the geological understanding for the new petroleum resource.

If all the latter are met, then the country might find the way for ensuring commercial domestic natural gas production. However, the society in the country needs to know the real potential for unconventional resource in the subsurface, which obviously is not immense or can perform high deliverability. Few local small "sweet spots" could be engaged for production (i.e. CBM – Mogilishte Fm. or Etropole Fm. (Stefanetz member)), but vast resource income and commercial flow rates are not expected, due to absent volumetric hydrocarbons in-place. The geological resource-forming specifications are present, with the good generation, accumulation and migration patterns, but nevertheless that fact; there is high risk of retention of the fluids in the trap structures (i.e. the case in the Devonian-Silurian black shales).

The U.S. shale plays, are an evidence for the sophisticated technological advancement in shale gas exploration, with the new multi-fracturing stages in the completion that comprise of 20 clustered hydro-fractured segments with pressure of the injecting fluids up to 600 bars. However, neither the onshore rigs in Europe are available, nor the shallower and geologically favorable shale reservoirs. The deeper sedimentary cover in Bulgaria governs for overpressured reservoirs, and with this comes the question if the hydraulic fracturing process can take place in such high pressure intervals (more than 700 bars)? If any attempt fails, or production commences with no preliminary assessments for the behavior of the completion process, implications such as chemical spillage or methane contamination of aquifers can derive. A necessary Environmental Impact Assessment (EIA) is deliberately needed before the production phase starts, which can determine whether the extraction will be a risk for the region or not. The dense natural reserve`s distribution (mainly in the mountain areas, but also in the BG NE and central Moesian Platform) from NATURA2000 framework, pose great subtraction of potential sites for unconventional exploration, due to restriction for operations in those region.

CHAPTER IV

10. Economical and environmental terms in the unconventional resources development of the U.S. and Europe

With the rapid onshore development of domestic natural gas production from hydrocarbon-rich shale formations (unconventionally), the exploration and production of such resource bring change to the environmental and socio-economical landscape in the areas of drilling activity for shale gas and oil. Questions have arisen due to the uncertain nature of shale gas production and completion technologies, along with the potential environmental impacts that such extraction could bring. Furthermore, the legislation and regulatory system coping with this development has the ability to prepare and distribute the certain objective source of information to policy makers, companies and in the society. This chapter will further discuss and try to answer some of the questions that have been discussed in the sector of natural gas production from low-permeable shale formations.

10.1. Economical aspects of unconventional petroleum resources

First of all, few important economic variables need to be clarified. Technical boundaries related with production of shale gas, non realistic break-even prices between the pioneer developer – the U.S. and Europe, different exploration costs and the economical value of unconventional fossil fuels, are all factors deployed not only in the global framework but on continental scale (North America or Europe).

In the global framework, a clear trend in the peak oil theory can be traced with the slow transition from the plateau stage in Hubert`s curve to the downslope, which has been expressed in declining flow rates with less new oil and gas fields` discovery. This is also true for unconventional resources, with their quick decline rates, studied recently (Hughes, 2012). The change in the supply source for oil and gas in North America, took an overturn from conventional petroleum reservoirs to shale gas and tight oil. The major factor contributing to non-proportionality in the resource base and the extraction grade between the two major resource (conventional and unconventional) is the energy returned on energy invested (EROEI). The lower EROEI for unconventional resources is due to lower grade quality of the resource and the larger costs for extracting it. Figure (67) forms a central, undisputed framework for all the current discussions of the economics and technological conditions regarding most types of energy resources.

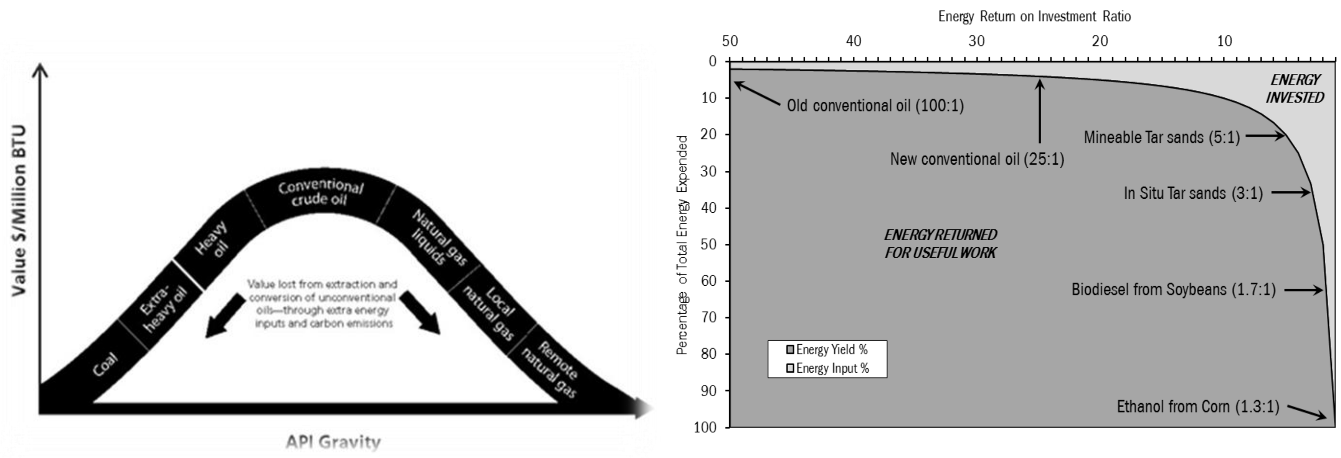


Figure 67 Hydrocarbon value hierarchy (left) EROEI ration for different deposits (right) (Statoil 2007 and Heinberg, 2013)

According to R.Heinberg (2013) the steep costs (EROEI) and the potential hazard for the environmental and human health emerging from completion and production stage of shale gas are the main misleading concepts in the development of unconventional fuels. Easy extraction of hydrocarbons (EROER of 70:1 to 200:1) is at its final marginal threshold. Along with that, the more companies deviate from conventional resource the lower the energy net return value becomes (Figure 67) with scarcer resource grade. On the other hand, extremely high or low values of API gravity (32<API<10) for a hydrocarbon deposits, lower economical value and diminish viability in terms of primary energy. Usual values of EROEI for continuous petroleum resource are 10:1 and 3:1. The economical charge of shale gas and other fuels of the same kind are marked by the “net energy ratio” and “net energy cliff”, which infer for the profitability mechanism of unconventional oil and gas extraction. Higher calorific value, ubiquitous existing infrastructure and easier extraction techniques with non-sophisticated technology, are all contributing factors for high net energy ratio for conventional resources. On the contrary, the increasing depth and cots for exploration in shale gas and tight oil, decreases the economical resources available in-place.

10.2. An “Unconventional” point of view for the shale gas boom

The current situation on the Earth’s future energy resource status is dominated by on the one side claims of a “Shale gas boom” versus the opposite view that this represents but another, very short-lived “Snake Oil” remedy, with no real power to change the overall development. This thesis would be remiss without a mentioning of this issue, but the debate is enormous, complex and fearsome in its intensity – the details of which lie outside the present scope. However, below it is represented a brief introduction to the strongly opposing disagreements between these two viewpoints.

As a part of a team of energy analysts and concerned retired petroleum geologists, Heinberg’s book “Shale Gas and Snake Oil”[1] (Heinberg, 2013) presents an overview of the high stakes involved in the current energy policy debate. He takes his point of departure from the finite fossil fuels resources (oil, natural gas, coal), which in the long run must follow the Hubert curve field depletion lifecycle, and eventually limit our increasingly energy-dependent future. This party in the debate is usually termed the “Peakists”. But, as the author explains, reduction of the use of fossil fuels is a most difficult proposition, because the big players, the oil industry, their banks and other involved institutions have a common goal: free and unimpeded fossil energy to the market. The view is that business as usual will not harm the planet, because there is still a lot of energy resources still buried in the ground. This party in the debate is usually termed the “Cornucopians” (after the mythical “Horn of Plenty”).

Heinberg foresees an imminent turning point in the debate, presenting public forum data and firm evidence for the “peak” of oil (which has already been passed) and natural gas production (best estimates put the natural gas peak in some 10-15 years), as well as what to him are irrefutable signs of the concurrent climate crisis in full development due to anthropogenic activity, mainly atmospheric CO_2 emissions. According to Heinberg, the oil and gas industry vociferously dismiss the concept that fossil fuels are constrained in Earth`s lithosphere, which is downright unbelievable for him. In fact his main objective with his book is to contribute evidence and facts with the aim of replacing the question: “*How shall we spend the newfound energy wealth*? (e.g. due to the shale gas boom) to: “*How should we reduce the CO_2 emissions in the atmosphere?*

Currently we humans are draining fossil fuel resources from the Earth with ever progressing rates, with the consequence that the quantity stored in the lithosphere for future primary energy consumption is already being consumed now, because of rapid of the ever-increasing energy needs in the developed societies and because of ongoing industrialization in many developing economies globally. Although no primary migration has occurred yet from the future source rocks (e.g. low-permeable shale formations) to conventional reservoirs, the new innovative drilling and “fracking” technologies have already begun rapid extraction from such deposits. The author presents the argument that the current consequences from this rapidly growing extraction rates is not reflected in the position of the industry involved, which rather is characterized by putting out misleading arguments instead of numerical facts.

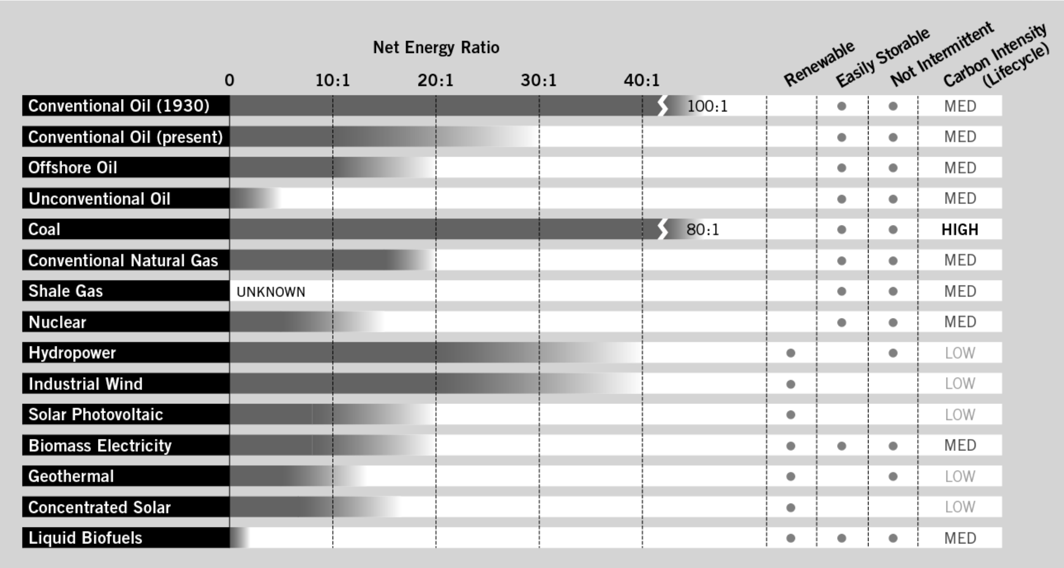


Figure 68 Energy return on energy invested ration of different primary and secondary energy fuels [1]

The exaggerated focus on the envisaged, but faulty, future production potential consumes a substantial part of Heinberg's book, in which he puts a special focus on the systematic denial regarding the very low energy returns of energy invested (*EROEI*) ratios for unconventional energy resources[1].

After elaborating the message that most of the Earth's super-giant oilfields are now depleted, and that we are currently experiencing declining rates of discovery of new oil fields (which are steadily becoming smaller and smaller), he focuses on the history and possible future trends, which will be characterized by soaring oil prices – the age of easily acquired hydrocarbons is ending. In this context Heinberg establishes an overview of the technological issues regarding the new energy resources – shale gas and tight oil[1]. The message is clear – the end of cheap oil and expanding rates of production is inevitable, it is only a matter of 'few years'. Societies will very soon have to focus on either on renewable energy sources (or on nuclear, wind and solar resource types, each with inherent pros and cons). If the decision is made to continue present day policies and to rely on more efficient ways of exploiting on-site fossil fuels, this must be done with dramatically reduced environmental impacts.

Expansion in unconventional gas production gave rise to concerns around the impact of operations in areas such as water, road, air, quality, seismic, and greenhouse gas (GHG) emissions (Howarth et al. 2011). As an example, the process of hydro-fracturing in shale gas wells causes additional GHG emissions compared to conventional gas wells. Taking into account the resulted CO_2 emissions from burning fossil fuels from both conventional and unconventional resources, the current climate crisis will be further urged. Unconventional natural gas development and extraction activities are most likely to add more CO_2 emissions in the climate, than to enhance the sink of greenhouse gases (IPCC, 2014).

Heinberg[1] illustrates and explains in some depth oil price fluctuations and the attending economical and financial instability, with the prominent example of the end of 2008, when prices reached almost $140 per barrel of oil. This was the time when the term "*peak oil*" went from being unknown, or only associated with 'conspiracy theorists' (Heinberg and colleagues have often also been termed "alarmists"), to being broadly familiar to everyone following the energy debate in the public sphere. It was exactly this oil price spike that led innovative drilling companies to develop and deploy the costly horizontal drilling technique needed for hydraulic fracturing, which made off-limit resources in shale formations available and technically recoverable for the first time. After only 5-8 years, this development overturned the coming natural gas supply crisis in the US, by now a historical event which is well documented.[1] The initial euphoria attending this technological development was immediately responsible by the „Shale gas boom" claims. Already now it is possible, at least according to Heinberg, to pass judgment of the validity of these claims however.

Here follows a brief outline of the findings and claims as to the future in Heinberg`s book[1]:

- The oil and gas industry`s recent unexpected successes will prove to be short-lived (a 10-year buble, instead of a hundred years of cornucopia);
- The long-term significance for the energy supply has been gravely overstated;

- The new unconventional sources of oil and gas production come with serious *hidden costs* (both monetary and environmental) that society cannot bear;
- The oil and gas industry`s exaggerations of the future supply potential are motivated by short-term financial self-interest, and, to the extent that they influence national energy policy, they will develop into a disaster for America and for future generations.

The environmental arguments, backed by economic data, are to him showing the likely brevity of the fracking boom. Two of his main arguments can be summarized:

- *Environmental arguments* – point to the consequences of significantly rising greenhouse gas (GHG) emissions from burning hydrocarbons. This includes rising sea levels (and acidification of the oceans), extreme weather conditions, and the likely exhibit of catastrophic impacts to agriculture.
- *Economic arguments* – highlight the inevitability of (near-future) fossil fuel scarcity as society continues to burn these finite, non-renewable resources in ever-greater quantities, and at ever-increasing rates.

The *clean* solution in both cases is found in other energy sources and by diminishing the overall energy consumption. Both of these imperatives are needed in order to curtail the very dangerous, steadily increasing atmospheric CO_2 levels.

10.2.1. Hydraulic fracturing and shale plays in North America

The main focus in Heinberg`s book (Heinberg, 2013) is the process of fracking – its nature, its technological requirements and its application conditions, along with the key cost per-well accounting. The statement that fracking will end America`s reliance on imported oil might be true, but only in the near decade. The extraordinary claims setup in the media all over the entire United States, that the country will soon become energy independent and that there will be cheap gas for a hundred years, will not play out as a true story. It is more likely, according to Heinberg, that reality will eventually, indeed soon enough, turn up to be another peak scenario which will proved right by the slow slide in production from shale deposits (Heinberg, 2013). The costs for hydro-fracking will be enormous as time goes by, making it more hard for oil companies to pay the leases and royalties to owners of the land, and for Wall Street to redirect finances to major stake holders. In stark contrast to the claims of a shale gas boom, Heinberg asserts "*We should prepare for life without cheap fossil energy*."[1] If you bundle many oil fields together the principle of tailing off production holds for all of them. There is always a need for further technological developments if you are to keep up a stable profitability. The new continuous oil and gas deposits extend differently in the sediment basins. The extreme lateral extension of the shale formations makes vertical drilling very uneconomical and very little efficient. This is why the combination of the horizontal drilling (so that horizontal layers can be tackled efficiently for more production) and the hydraulic fracturing technology (increase the flow of gas, by pressurizing the formation and causing artificial fractures, which are suited for migration paths of the gas) made it possible to harvest hydrocarbons from formations no one considered could be exploited.

Hydro-fracturing first become famous and widespread within the petroleum industry during the 1970`s in efforts aiming at "enhanced oil recovery" (*EOR*) in conventional oil and gas fields. However, oil- and gas-bearing shale rocks remained mostly out of bounds for drillers. In the 1990`s an important discovery was made – natural cracks and fractures in shale formations are occurring in-situ. If "fracking" could be applied where cracks are already present, large amounts of gas might be released. The bending of the well accomplished the continued contact between the well bore and gas-bearing strata, and allowed producers to drill below public buildings and restricted land areas.

After this drilling innovation, the "*slick-water*" agent in fracturing was developed, which is made by adding friction-reducing gels to injected water, to increase the fluid flow in fractured rocks and wells. The first time where the two technologies were combined was in the famous development of the Barnett shale formation in Texas. In time the constituents involved and the fracking agents and fluids became a much more complex mixture of chemicals, which today is a carefully guarded business secret. Still some of them are well known, due to common use in the petrochemical or domestic utilization (Figure 69).

The main difficulty in shale reservoirs` exploration in North America was the heterogenicy in the deposits that could vary even over small distances (300 m or less). Thin laminated beds of shale follow moderate constant patterns in horizontal direction, but alter abruptly in other lithotypes vertically. After the kick-off point in a vertical well, the bigger contact with the planar direction of the well can be obtained. The enhanced natural fractures done by shattering the rock should be kept open after the fluid injection, which is usually accomplished by a proppant or other granular material (ceramic, bauxite, etc.) deposited perpendicularly to the beds fissures. This further requires the injection of a viscosity-regulating fluid with the sand (proppant) to achieve settling of the suspended mix when pressure is reduced. Backflow fluid from fracking, in nowadays is usually reinjected in the formation, stored in pits, or sent to water treatment plants.

The last key technology of modern fracking, established as late as in 2007, consist of multi-well pads, or cluster drilling, during the exploration and production stages, which e.g. allows the option to drill 16 wells from one platform.

Chemical	Use	Consequences of not using chemical
Acid	Removes near well damage	Higher treating pressure, slightly more engine emissions.
Biocides	Controls bacterial growth	Increased risk of souring the formation (H_2S gas from sulfate reducing bacteria growth) and increasing corrosion.
Corrosion Inhibitor	Used in the acid to prevent corrosion of pipe	Sharply increased risk of pipe corrosion from acid. Well integrity compromised.
Friction Reducers	Decreases pumping friction	Significantly increases surface pressure and frac pump engine emissions.
Gelling Agents	Improves proppant placement	Increased water use. Natural gas recovery may decrease in some cases by 30 to 50% where frac fluids must be gelled (conventional fracs).
Oxygen scavenger	Prevents corrosion of well tubulars by oxygen	Corrosion sharply increased and well integrity (containment) compromised.

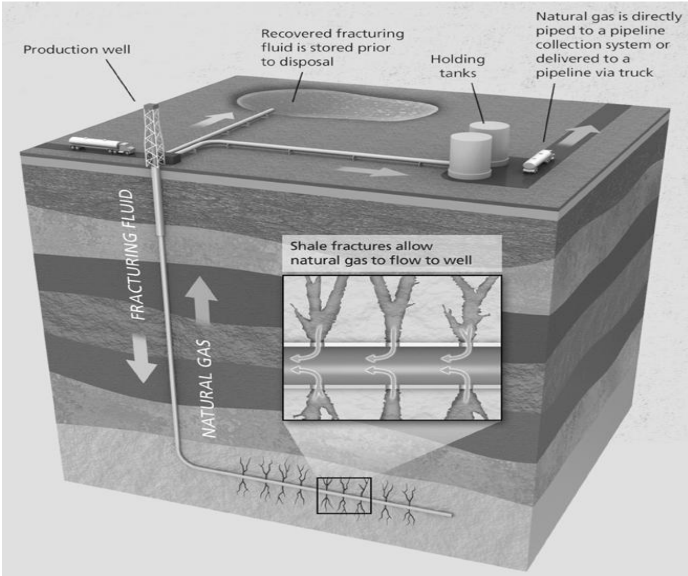


Figure 69 Chemicals used in shale gas fracturing and the consequence if such are absent (left) and schematically explained depiction of the life-cycle of a completion stage, including the hydraulic fracturing (right) (Heinberg, 2013)

The sequence of shale gas exploration and production is comprised by the following main activities (in the United States) (Figure 69 right):

- Initial geological survey, identifying the core area in the shale gas/tight oil play (e.g. Marcellus, Bakken), with the aim to locate the "*sweet spots*".
- Acquire proprietary drilling data and drilling own test wells for interpretation of well logs, core samples, seismic profiles in the concession area. 3-D seismic data from companies will enable visualizing of source rocks with high TOC and the extent of hydrocarbon generation area
- From a regulatory point of view – the company is compelled to have drilling leases, purchased from landowners, for exploiting subsurface mineral resources (this system differs from the one in Europe, where typically it is the national governments who owns the rights over mineral resources at depth).The lease agreement should include the right to build drilling pads, buildings, roads, pipelines and etc.
- Planning for drill site usage must include the fluids to be handled at the wellhead, either gas or oil (if there are volatile hydrocarbons, then pipeline construction to downstream market consumers and companies should be constructed). Drilling depths can reach 4000 m and can take up to several weeks.
- After drilling operations, when the completion stage begins, the well should, in principle, be cased with steel pipe strains and cemented to some extent, or along the depths in which there might be hazardous interaction with viable aquifers. This is meant to protect groundwater from contamination with methane and stabilize the well for the next stages of the process.
- A perforating gun is lowered to the deepest portion of the well, which intended to punch small holes in the casing of the horizontal well section. Once this is done, a flushing system is needed, making use of acidic chemicals to help unclogging the perforated holes, so the gas in the shale matrix can more easily flow into the wellbore.

- Now hydraulic fracturing can commence. Large pumps drive millions of liters of water mixed with "slickening" agents down into the horizontal part of the casing, forcing and pushing the water outwards which will then produce hairline cracks in the shale (*fissures*). Then the sand used as a proppant is injected, which in the U.S. is mined and transported several thousand miles away from the source (Heinberg, 2013).

When you multiply the procedure the thousand times, you will derive with the number of drilled wells from several well-pads (onshore rigs) in the Marcellus shale, which has estimated around 160 rigs in 2014 (Nash, 2014) (Figure 70)

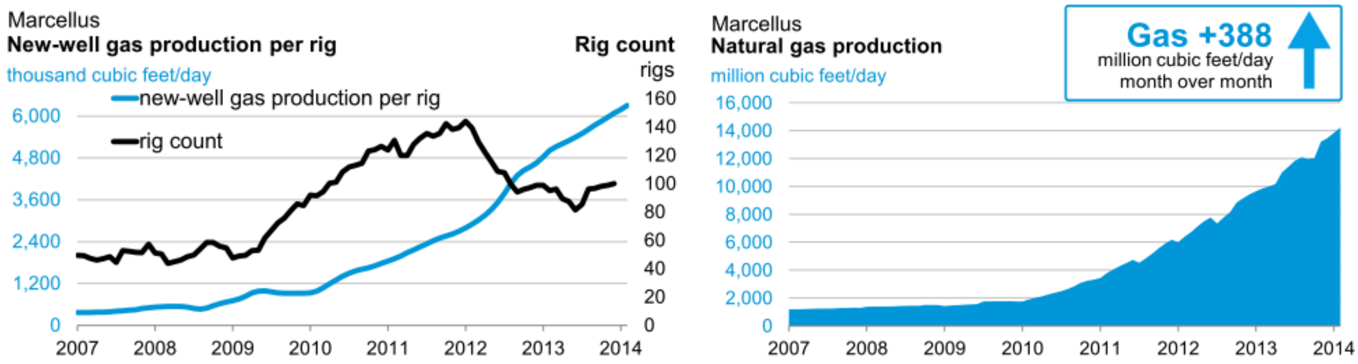


Figure 70 Marcellus gas production in 2014 (left) and gas production of new wells (right) (Katelyn M. Nash, 2014)

The biggest shale play in North America is strongly believed to be the Marcellus Shale Play. It is positioned in the most important oil and gas provinces in the U.S. – The Appalachian Basin. Above a pre-Cambrian crystalline rock lies a thick Paleozoic sediment succession that reaches 12 km in depth. The Middle-Upper Devonian part (350 Ma) of the sediments is 1100 to 2800 m thick, in which the lower part (305 m thick) is the organically-rich one, comprising of black shales and deltaic sandstones. These lithotypes are considered as main hydrocarbon-generating rocks for conventional oil and gas and continuous petroleum yield potential. In the very same Devonian Shale for the first time a shale gas well was drilled, dating back from year 1821. The location of Marcellus Shale spreads below the land of five states, namely – West Virginia, West Pennsylvania, New York, Ohio, and Maryland. The overall area estimated for the play covers 95 000 mi^2, which several times more territory than the Barnett shale play. This shale was estimated to have the quantity of TRR - 262 TCF (Katelyn M. Nash, 2011). Some 80 companies struggled to find a spot, and are now currently operating, in the Marcellus Shale Play (Table 19), some of which include Chesapeake, Chevron, Anadarko, Longfellow and True Oil. The play currently hosts 3850 operating wells with a total production in the vicinity of 5BCF/day (Heinberg, 2013). Declining of produced quantities of hydrocarbons from all those boreholes is depicted in the downward curve of the Figure below (Figure 71). A decline rate of 95% over the first 3 years of exploitation in Marcellus were calculated (Hughes, 2012), whereas the EUR was evaluated to be 1.16BCF (USGS, 2012).

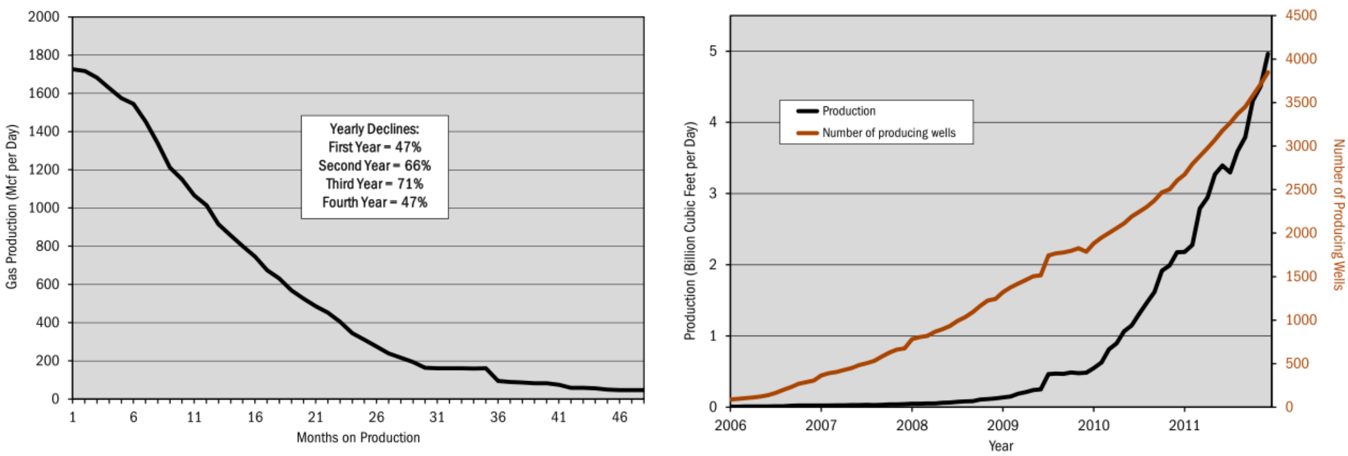


Figure 71 Type decline curve for Marcellus Shale (left) and shale gas production and number of producing wells in the Marcellus shale (right) (David Hughes, 2012)

Mean initial production (IP) for Marcellus is given to be 1947 MMcf/day with average well production at 1290 MMcf/day (Hughes, 2012) (Figure 71). Furthermore, when the decline curve in Marcellus is linked to the decline rates in Barnet (39% from the first to the second year) and Haynesville (48% annual decline rate), strong evidence for underperforming production tendency of shale plays is established (Hughes, 2012). Moreover, Eagle Ford showed decline rate results of 76% of average oil decline and 60% for the gas one (Gray Swindell, SPE, 2012).

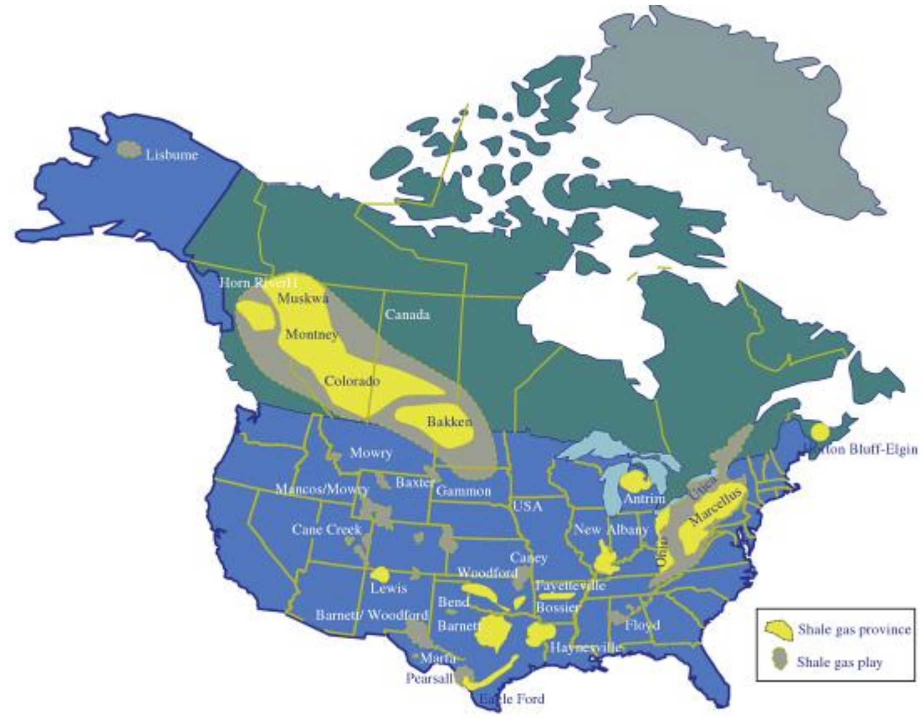


Figure 72 Sketch map of major shale basins in North America (EIA, 2011)

The main shale plays in the United States (lower 48 states) that are of commercial importance encompass the following – Barnet, Fayetteville Shale in Arkansas, Haynesville, Marcellus, Woodford, Eagle Ford, Bakken and Utica (Figure 72). Except those, some 50 basins are found throughout the whole U.S. and west Canada. The proliferation of drilling in those shale formations (50000 wells until February 2013) along with the increase of domestic methane production (to 9.6TCF) was until the year 2012 (Cainengzou et al, 2013). The main volumes of gas recovered on a daily basis have risen to 10BCF in 2010 for all of the U.S. (Figure 73).

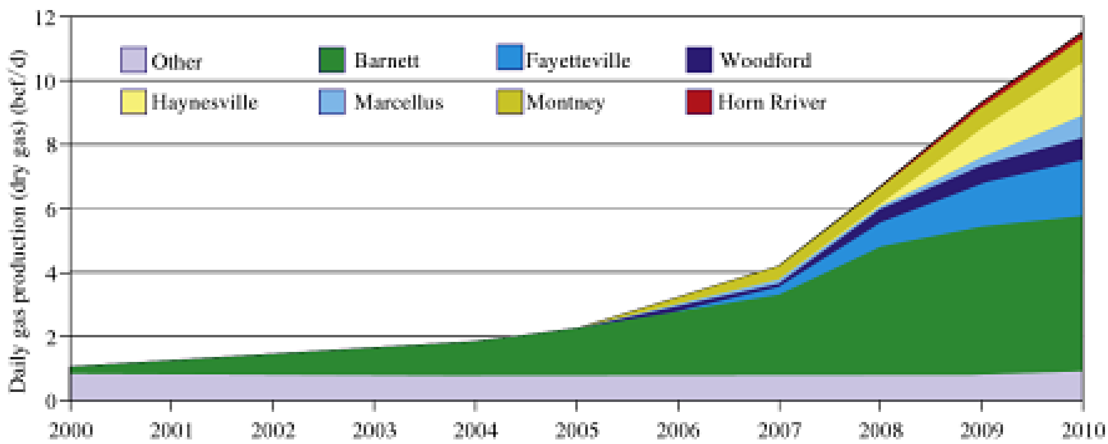


Figure 73 Shale basins on the territory of the United States (Cainengzou et al. 2013)

A comparison between the crucial and most important gas- and oil-bearing shale plays in North America and some analogues from Europe is summarized in the table below (Table 19).

Table 19 Summary table with reservoir parameters, drilling data and geological specifications of some shale plays in North America and Europe (after J. David Hughes. (2013) Book "Drill, Baby, Drill")

Country	Play	Thickness (ft)	Depth (ft)	Ro (%)	TOC (%)	# of Wells	PR*
United States	Barnett (core area)	100-600	6500 – 9000	2.1-2.3	3.5 - 8.0	15000	5.85
United States	Barnett SW-West	100-250	6500 – 9000	2.1-2.3	3.5 - 5.0		
United States	Woodford	120-345	6500 – 13000	1.1 – 3.0	3.0- 10.0	3129	3
United States	Fayetteville	20-200	1000 - 7000	1.5 – 4.0	4.0 - 9.5	3873	2.8
United States	Haynesville	200-300	10500 – 13500	0.9 - 2.6	3.0 - 5.0	2800	7
United States	Marcellus	50-200	4000 – 8500	1.0 - 2.5	2.0 - 10.0	3850	5
United States	Antrim	70-160	600 - 2200	0.4 - 0.6	1.0 - 20.0	-	-
Germany	NW Posidonia	50-200	6500	0.48 - 4.8	2-15 (11mean)	-	-
Netherlands	West Epen	50-82	4900 - 21325	1.65 - 1.85	8.0	-	-
Poland	Baltic Depression	> 328	8200	1.5	7- 14	-	-
Poland	Lublin Trough	325 - 650	7545	1.4	0.5 - 1.2	-	-
Denmark	Alum Shale	147-580	4300 – 21540	0.5 - 2.4	2-17 (mean 8)	-	-
Bulgaria	Etropole	260-650	5000-16400	1.15	3.0	-	-

*Production rates in bcf/d

But what is a typical example of a shale gas boom? Another question, for which Heinberg expresses an answer, as his book continues the revising of the concise shale production period. A typical example followed in the boom of shale industry is a typical town called Desdemona, which from a flourished oil and gas industry place in Texas around 1918, turned into a typical case of the retrograde development: "*boom goes to bust*"(Heinberg, 2013). Until after the local "peak oil" stage in 1930`, the government of the city of Desdemona started to disassemble public activities, ending while its lone school closure in 1969. Following this pattern, a city once known for its strong economy due to oil and gas reserves, now vanishes from the map of Texas, becoming a "*ghost town*". The lessons that should be learned from such a case are that often financial speculations based on deliberate or extravagant overestimation of resource, sets the bar of the peak oil so high from the baseline, that the bust that follows inevitably will be even more destructive (Heinberg, 2013).

In the history of mankind, most of such commodity booms were associated with gold, silver, oil, gas, and coal resources. If we look closer in those, we can conclude that all of them are primary energy fuels or mineral resources with substantial value. Some of the involved individuals, agencies, companies or local governments still say that "*This time will be different*"[1] , and especially in regard to the current 'shale revolution'. The truth is that instead of learning from our mistakes, we keep repeating them over and over. The current boom, what has been called the "*fracking frenzy*" (Heinberg, 2013), is so immense and unseen in some states like Texas, North Dakota, Oklahoma, Louisiana, Arkansas, Colorado and Pennsylvania, that it appears to be completely inconceivable that it could end as a similar collapse.(Heinberg, 2013)[1] This is spite that some strongly worrying signs are already starting to appear in the shale gas and oil industry: declining flow rates; low recovery rates; unfulfilled resource assessments; lower estimated ultimate recovery per well (EUR) than foreseen; environmental disasters linked with irresponsible storage of wastewater fluids on the shale play site (Colorado, severe rain-induced floods). Initial production rates (IP) are not as high as expected, and even the declining rates that follow can reach 25% of the total produced hydrocarbons as in Haynesville shale play in Louisiana (Heinberg, 2013)[1]. To Heinberg it appears clear that the monopoly of oil companies suppress the stand of the "*peak oil*" camp. The myth of the next 100 years of abundant gas supply, extracted from suitable shale formations is much more based on self-interest on behalf of industry, media and politicians, than upon realistic documentation (Heinberg, 2013).

Some companies from the oil sector (*BP, Exxon, Chesapeake*) state that unconventional shale gas and shale oil, might herald a new century of energy abundance, and even claim that a whole fossil fuel independency can be fulfilled for North America`s supply[1]. Nevertheless, most of the public analysis *(EIA Annual Outlook)*[3] show clearly that the production history, economic, environment and geological constraints of those resources in the US show that they will soon run out, or fall abruptly, because of two reasons : (**1**) shale gas/oil wells deplete quickly, and no new major fields will be discovered, which will lead to total declining of per-well productivity, and some of the fields might become only an "*exploration treadmill*" resources with maintained production (Heinberg, 2013); and (**2**) most of the unconventional resources (tar sands, shale gas/oil, oil shales, tight gas, CBM) require enormous cost-intensive strategies supported by vast amount of expenditures, that are consumed by the sector in its exploration and production stages, which accounts for impossible scaling up of production to market levels. This pattern of poor forecasting is still characteristic today, as is further researched in this master thesis.

At the moment shale gas is providing some 40% of the US total natural gas production[2]. Only six of the big shale plays account for 88% of the total production (Heinberg, 2013), with each play constrained by its own "resource pyramid", and the smaller areas covered by *sweet spots*. The vast surrounded areas can contribute only relatively minor offset productions and marginal rates. The core areas are always the most producible spots in any shale deposit, so once these are exploited, drillers will have to deploy their equipment further away from the high productivity spots, and each next well will have lower recovery rates than the previous one (Figure 74). The claim from the oil and gas companies that the U.S. have gas for 100 years is based on EUR estimations for single wells, which is not in any way a favorable methodology for assessing continuous deposit accordingly to D.Hughes (2012).

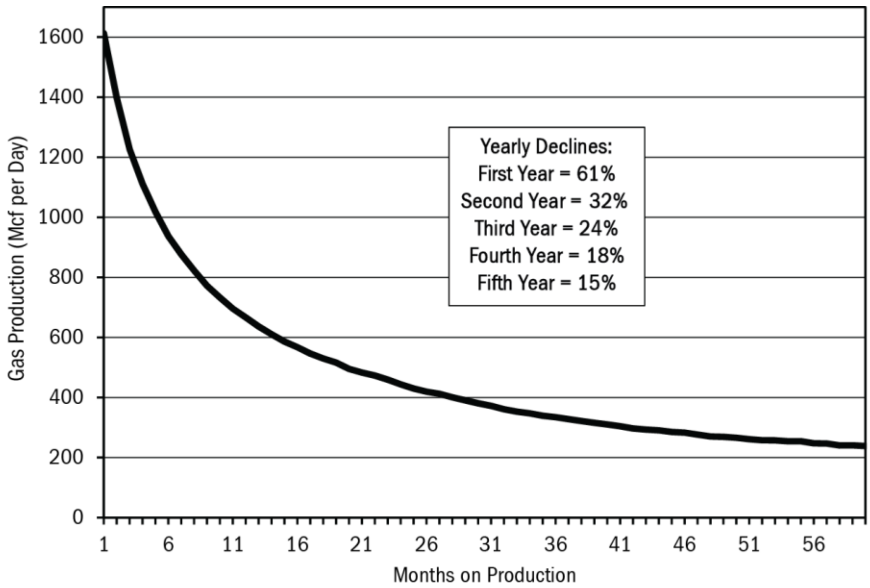


Figure 74 Decline curve rate in total gas production in North America (David Hughes, 2012, Book)

In order to keep the offset production from the declining rates in shale gas wells balanced, much more drilling needs to be deployed in order to sustain the total output production rate at a steady (plateau), or slightly growing rate (Heinberg, 2013). 30 to 50% of the shale production in North America should be replaced each year, which will result in some 7200 new wells per year (J. David Hughes, 2013). And those numbers will just keep the gas and oil flowing. (Heinberg, 2013) refers to this as the "*treadmill to hell*". Maintaining the current production rate of shale gas will eventually need even higher input efforts. The number of gas wells in the US in the year 2000 were in the vicinity of 341,500 (J. David Hughes, 2013)[2], which is an achievement that took almost a century. With the low natural gas market prices in 2012 *($4 MMBt*u), current revenue may accounts for just 33$ billion per year[2]. This huge cost-intensive capital gap is filled with *asset sales* and *higher production of liquid fuels*.

Considering how reliable (unreliable?) current shale gas resource estimates are, it can be concluded that most of the numbers are not complying with the baseline, or not fully adequate. There are some terms that need to be clarified so that a better perception can be made with respect to shale resources:

- Resources are immense – no doubt in that – but a resource include also the ultimate percentage of hydrocarbons that are uneconomical for extraction, as well as those parts of the oil or gas resources that are technologically impossible to reach (at least at present).
- Reserves are always the more decent percentage of the total resource base.
- Technically recoverable reserves (TRR) are the resources that theoretically could be extracted given current technology advancements, thus they are in the vicinity of the full quantity of the gas that might reach the wellhead.
- The smallest category consists of economic reserves – resources that can be extracted with the current technological level, and which are in compliance with the plausible, current downstream market mechanisms and price rates.

If/when prices of natural gas again turn high(er) more resources will be classified in the economic reserves category. This is usually left behind in the official assessments from some of the agencies[1], and people are led to believe that shale gas resources may all be produced at the current extremely low gas prices, which are so low that even some power generation stations or millions of cars and trucks can be run on natural gas.

The U.S. Energy Administration states that the technically recoverable reserves in the U.S. from shale gas are 600TCF which is sufficient enough for 24 years of supplies at the current consumption rates[1]. But even those numbers are quite aggressive in their forecasting, because most of those resources are *unproven* and they are not likely to reach the same rates of drilling and production as from the sweet spots. Furthermore, high declining rates of course lead to decreasing recovery efficiencies. The recovery rates are about 7% for the unconventional resources[1]. This suggests that the estimate of technically resources for the US shale plays will be around **240 TCF** (IPC), which entails only **10 years** of current natural gas supply for North America (Heinberg, 2013)

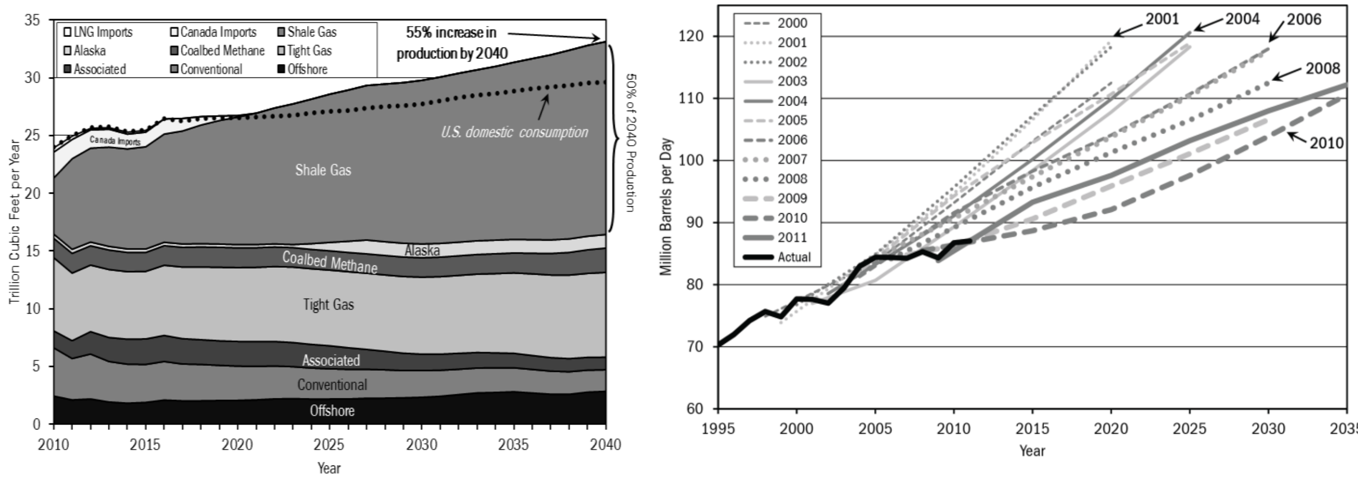


Figure 75 Prognosis for production rates of natural gas derived from different primary resources – conventional and unconventional (left) and projections is yearly baseline with trends for future production of oil per day (Heinberg, 2013 and David Hughes 2012).

If we follow the tight oil production trends, the situation might become quite similar. The mirrored aspect of shale plays like Bakken and Eagle Ford (North Dakota and Texas), lies in the per-well production decline rates of up to 90% in the first two years. The tight oil play of Eagle Ford is younger in production than Bakken, which means that the operators drilling in Eagle Ford are still experiencing high production rates because of mobilizing from “sweet spots” in the core areas. But it turns that *even today*, Eagle Ford declining rates are higher than the one`s in Bakken (Heinberg, 2013). This will put most of Eagle Ford wells into the “*stripper*” category (yielding less than 15 bbl per day)[1]. A peak of production in this field is anticipated already around 2016 with almost 900 000 bbl per day (J. David Hughes, 2013). Total oil recovery is expected to reach 2.23 billion bbl by 2025, amounting for only five months of US consumption.[2] Today around 80% of the tight oil production in North America is composite from these two fields. A new player currently emerging is the *Monterey shale* in California, which is assessed to constitute 41% of America`s tight oil resources.[1] Even though at the surface encouraging, it seems that more than 600 wells turn out to yield less than 15 bbl per day/each, because of complicated geology – faulted, folded, and fractured, which requires sophisticated studies and technology with slow production rates (J. David Hughes, 2013). The total technically recoverable unproved resources are in the range from 23 to 34 billion bbl[1]. This presents only three to four years of consumption (Heinberg, 2013), which is way off too low from the point of the alleged “*energy independence*”.

Unconventional resource in the global outlook

After introducing the North America`s ‘shale revolution’ and current status, Heinberg redirects the focus of the future shale development outside North America[1]. A similar liberation of oil and gas from similar reservoirs around the globe is met with skepticism, when he (Heinberg, 2013) looks at the greater overview, and the factors affecting the triggering of the shale technology.

- In *Europe* – as already discussed in *Chapter I and III,* countries like Bulgaria, France, and Luxembourg have enacted *bans* on fracking for environmental reasons. In other countries, other types of regulations constrain drillers from production (UK, Germany, and Poland). The social and public opposition against fracking has a strong base in Europe. According to EIA, Poland is highly possible to have reserves of shale gas accounting for 187TCF, and takes the position of main player in the European shale gas transition. However, as in the US case scenarios, the number seems to be diminishing with the progress of revealing new geological data in the country – e.g. USGS estimated recoverable reserves` base (TRR) of 1.34TCF (mean) for the Polish-Ukrainian Foredeep basin (Lublin) in their recent assessment from 2012.

- *China* – has probably even larger reserves than the US, but high clay contents in the shale plays makes them less apt to fracturing because of adverse geo-mechanical properties. The shale deposits are deeper, requiring high well investments. China lacks means for compiling, assessing and sharing geological data, compared to the US.

Critical factors and obstacles for shale gas` penetration the worldwide market are expected to be several:

- Lack of drilling rigs outside the US – in the moment around 1,200 rigs are situated in North America coping with 19 shale plays, while in Poland for example there are only half a dozen rigs;
- Lack of geologists and engineers outside North America in the field of shale gas production;
- Water demand for completion activities – Saudi Arabia has a scarce water resource, even there are many gas-bearing deposits on place. Also the increasing climate change`s extreme weather patterns now bring drought to many areas in increasing frequency;
- Geological problems – adverse shale lithology formations might cause problems for fracking.
- Financial factors – in the US development the industry was balanced by capital from big investment banks, which hyped the prospects for cheap oil and gas energy in the near future. In other countries, state-owned companies drill and "*investment decisions are made by risk-averse bureaucrats rather than risk-seeking capitalists"*.(Heinberg, 2013).

10.3. Potential environmental impacts during completion and production stages in shale gas production

Hydraulic fracturing impact can be seen in both micro- and macro-scale all over North America. In the micro-scale overview, all the potential hazardous influences on the environment and the human health are included. Because of the huge scope of the findings and environmental concerns derived from fracking, only in brevity some will be discussed, whereas the others will not be present in the report.

10.3.1. Water management during completion operations in shale gas production

It is a proven fact that hydraulic fracturing does take immense quantities of water that ought to be pumped under high pressure in the reservoir. More than 60 million gallons may be required for a single well-pad cluster, where the water obtained should be provided from the leased property, sucked from rivers or lakes nearby or bought from municipal water systems. Some dry states in the southwest part of North America require provisions of water (as an example is the Colorado River serving as a source), which makes the drilling cost-intensive. Most of the wastewater from the process is stored in open pits, but along with it are carried some chemicals like carcinogenic benzene, radioactive elements (NORM) such as cesium and uranium, and the less hazardous corrosive salts. No matter what the treating procedure (if any) or the reinjection is, still high risks for human health exist. The backwater flow from the fracking process can endanger streams, rivers, and impact waterways with high amounts of TSS (Total Dissolved Solids). Moreover, this can cause oxygen depletion in water basins, temperature rise and reduce the transmission (block sunlight) of water. Wastewater from fracking since year 2011 is considered as too radioactive to be dealt with in a safe manner by municipal water treatment plants, which legislation was introduced and attributed to EPA (*US Environmental Protection Agency*)[1].

In another aspect, groundwater is at high risk of contaminating during hydraulic fracturing process (including the artesian springs and shallow aquifers). Even if the well is constrained by the casing and the cement layer, this might not stop the diffusion of dry gas (CH_4) into other formations and stratigraphic levels. Cement shrinkage is the most frequent failure of well preparation. The leakage of methane can cause distribution of the gas all the way to the residential drinking water system.

10.3.2. Air quality disruption due to shale gas production

Methane released from the drilling and production of shale gas wells reacts with atmospheric hydroxyl radicals (OH^-) to produce water vapor and carbon dioxide, thus having a main impact on the climate by absorbing the long wave lengths of the sun and heating some of the atmospheric layers.

Other undesirable or heavier components of natural gas could be hydrogen sulfide, ethane, pentane, benzene, emissions from trucks, pumps, compressors and other volatile organic compounds. The drilling activity and intense traffic can cause high dust levels in the air. Wastewater retrieved from fracking operations contains ozone. Once it starts to evaporate from the evaporation ponds/ storage pits, it comes in contact with diesel exhaust and causes lung infections, coughing, chest pains and asthma[1]. Another probable issue is the lack of pipelines in North Dakota, which accounts for just flaring the methane from a huge stack into the atmosphere.

10.3.3. Consequences from using fracking on the leasing land/area and heighten seismicity concerns

Drilling for shale gas and tight oil can harm the land through the soil, water, damage vegetation, livestock and wildlife, or simply erosion and earthquakes. Heavy metals like lead, mercury, cadmium, chromium, barium and arsenic have a trace signature in soils near well pads (Heinberg, 2013). In the mountainous regions of the Marcellus shale, drilling leads to erosion where loose sediments can enter the surface streams and contained the fish habitats and drinking water sources.

Weak seismic activity from hydraulic fracturing is not experienced from the human body during the process, because of the lower rate and frequency of the vibrations, but number of quakes cause damage in non-seismic zones like Colorado, New York, Arkansas and others[1].

10.4. Conclusion and Alternatives for energy production

The other real impact of fracking on the nation is at the macro-scale of energy policy in North America. The US is failing to plan its future which will be characterized by scarce hydrocarbon resources and with a clear need and focus on a substantial renewable energy resource base[1]. Failing to do such a transition is failing to do what every nation must, according to Heinberg. He ends his book by stating that failing to take this responsible action in order to survive in the coming next century of sharply destabilizing climate patterns is <u>not</u> an option, but a reduction in the dependency on fossil fuels <u>is</u>.

There are two main risks in the oil and gas industry in the US at the moment: <u>price volatility</u>, which will affect the profitability of shale gas and tight oil well, and <u>liability with respect to environmental and human health damage</u>. High fuel prices can give shale gas an economic sense, but no one can predict the price and its stability in the following decades, as has been amply demonstrated regarding the fracking boom (Heinberg, 2013). And even though improvements in protection of the contamination from fracking are developed, some counties are banning the process based <u>solely</u> on concern for human health. This results in sharp decline in potential revenues for operators, a drop in stock value and an increase in borrowing costs.

Other unconventional resources like methane hydrates have EROEI as low as (*2:1*) and the technology for its potential extraction is currently so undeveloped, that in the near future there will not be a chance for their exploitation at the scale needed were they to constitute a serious contender to fossil fuels[1]. Immense deposits are situated in the West Pacific around the coastline of China and Japan. Another aspect is the *oil shale*, or kerogen, in Utah and Colorado. The US has the largest deposits of those resources in the world amounting for 4.3 trillion bbl of oil equivalent[1].Canada`s tar sands (bitumen, oil sands) are an economic resource, but again with a very small EROEI (*3:1*)[1]. Only because oil prices are quite high, are tar sands currently profitable (synthetic crude made from bitumen).

Based on the above summary and comments of Chapter IV to the arguments in Heinberg`s book, the transition between fossil fuels and renewable energy sources is advocated to be as fast as possible. The EROEI for most renewable is demonstrably lower than the historic very high energy profit ratios for fossil fuels (Figures 67 and 68), but EROEI for oil and gas is now inevitably declining, while it is improving for wind and solar power. The largest source of renewable energy in the world at the moment is hydroelectric power. But even these are not without environmental issues; building dams create potentially huge environmental problems, if not addressed properly already in the design phase. Biomass might be a local and regional solution, but is nowhere near to be able to compete on the global scale. Here wind energy may stand a better chance, but primary capital investment for wind power is substantial.

Solar and nuclear power are both technically challenging options for our societies onwards, but both are viable alternatives, however each with their specific issues which must be solved before global use can be contemplated: Solar power will be dependent upon the 'intelligent grid', which needs to be able also to store the energy carried and distributed. Nuclear power (breeder reactors and/or Thorium-based fission) face severe demands regarding safe storage of radioactive waste products; routine, wide-scale usage is neither without serious security issues as well.

It is not the objective of Chapter IV to point to all energy resource alternatives, and far less to a general solution to the coming global energy demand crisis (if one is in agreement with Heinberg). But it must be characterized as irresponsible were the scope, facts and analysis in Heinberg (2013) to be disregarded, or banned, from serious attention. Everybody working outside, as well as within, the oil and gas industry, has an obligation to assess the value and merit of the issues raised; hence the perhaps slightly provocative "Snake oil" tag to this thesis.

Thesis`s Conclusion, Discussion and Final Remarks

The thorough analysis of pore spaces in tight organic-rich shale reservoirs, resolved in understanding the problem with gas storage depots and nano-meter throats in those confounding beds. This infers, that the resource management of evaluation procedures, it strictly obeying and in relationship with the amount of larger pore sizes (>200 nm), low stress gradients (elastic and strain), methane sorption properties, organic richness and maturity level. Each one of those can affect the overall resource deemed to be prospective. Furthermore, the range of the nano-meter scale and its flow regime patterns (slip flow), should be accounted for in any unconventional resource evaluation method. SEM images reveal the needed explanatory evidence for the nature of the tight pore network, where such should precede every rigorous resource in-place abundance calculation for shale gas reservoirs. The difference in the permeability is likely to be affected by the molecule size of the fluids, gas sorption in the matrix, and slip flow phenomenon. Shale reservoirs can constitute of sub-nanoDarcy to micro-Darcy pore systems, which are highly linked with the rock`s deposition properties – moisture content, anisotropy, effective stress, permeating fluid, and salinity in the pore fluid composition. Even if GIP resource for shale and mudstone reservoirs are considerably high, economic production rates are technically difficult to achieve, due to lack of information and researches for the fluid transport processes in the matrix, nano-scale throats, and fracture systems of the lithotypes. Declining rates, that were observed after year 2011 in some major shale basins in the U.S., are a result of the phenomenon of limiting the long-term gas flow rates because of the matrix transport system, even if natural fractures are enhanced. Among the controlling factors for achieving commercial production of shale gas, are the storage space, gas capacity, and transport and migration properties along with the amount of gas present in the shales (GIP). However, the storage mechanisms and migration flow regimes are still not well understood, which alters the amount of extractable gas that can be projected preliminary

This thesis should be viewed as a multi-disciplinary investigation of the resource abundance of shale gas resource and their potential impacts during such production for the environment and the human health. A confirmation for the resource calculation methodology was corroborated with the calculations for Denmark with a combination of independent collected data and geological information. The rigorous and optimal values for the recoverable reserves of Denmark (**22.5TCF**) do express a result positioned in-between the EIA (31 TCF) and the USGS (6.9 TCF) for the recoverable reserves of Alum Shale in the country, which is still deemed as slightly larger amount or resources than what is expected for production.

The models for the prospective area adopted and re-evaluated from the United States Geological Survey (USGS) and GEUS for the Danish Alum Shale, were deemed accurate and to the point. In addition, the recent assessment of USGS of the recoverable potential of shale gas in Alum Shale (Gautier et al., 2013), has its solid scientific background with the forecasting model, Monte Carlo simulation, per well EUR and drainage area and theoretical production from tested and untested cells in the AUs, included in the their assessment. This infers for the most accurate (mean) number that this study redirects to. The combination of the incremental use of the two assessments (ARI and USGS), with the polygons and prospective area with EUR values from the one and the reservoir engineering calculation`s equation for the volumetric per-well evaluation form the other, proved to yield realistic numbers in the magnitude of the real volume of hydrocarbons in place in the evaluated formations. Furthermore the ration for the free and adsorbed gas was a fundamental for the interactive model for the proportions of free and adsorbed gas in Alum Shale.

The contrast in the two case studies – Denmark and Bulgaria, was obvious in regard to the approach and geological information acquired. Even though, the abundant geological information summarized for Denmark, no production testing yet exists in the country, which will change significantly the numbers of GIP, once more than scientific wells are drilled in North Julland. On the other hand, the lack of geological data and information for the Lower Carboniferous hydrocarbon prospective in Bulgaria urged for own scientific investigation, which led to the collection of several samples from the Lower Carboniferous. The SEM analysis conducted, revealed probably the gas capacity is increasing with the order of increasing the number of the kerogen type (I<II<III), which was attributed to higher capacity of vitrinite, instead of other macerals. The sorption capacities are thus also higher in the shale/siltstone and coal samples, due to abundance of vitrinite. The constructed polygons for the depths of the C_1, the potential net-thickness of the shale beds in Konarska and Trigorska Fm., and the evaluated petrographic and nano-scale properties of the lithotypes, concluded in quick and raw assessment of the in-place resource. The derived number of 52TCF on a core area of 3200 km^2 constituted for huge resource potential in the Lower Carboniferous succession, which is likely the maximum and overstated amount. Although, 50% methane gas was encountered in sample BG1.1-J1, the pyrolysis analysis` response inferred for pre-mature to immature sample level.

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