Recovery of Lignin Derived Phenolics by Liquid-Liquid Extraction

Master Thesis Project

K10og-5-F16

Aalborg University Esbjerg
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Title Sheet

Master Thesis

Thesis Title:	Recovery of Lignin Derived Phenolics by Liquid-Liquid Extraction
Group:	K10OG-5-F16
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Supervisor:	Marco Maschietti
University:	Aalborg University Esbjerg
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Initial Problem:	Hydrothermal conversion of lignin as a viable process to produce fuel and valuable chemicals. How can the extraction of phenolic components from an aqueous stream add value to the process and make it more economically feasible?

Student:

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Abstract

The main focus of this project was the extraction of phenolic components from an aqueous stream that is generated during the hydrothermal conversion of lignin to bio-oil. Since water is utilized as a reaction medium in this process, a large amount is used continuously and it has to be recirculated. The water ends up containing high concentrations of phenolic components like guaiacols and catechols that are valuable chemicals for the industry. This fact provides an opportunity to recover the phenolics and add value to the conversion process of lignin. The recovery of the phenolic components from the aqueous phase can be considered a part of the optimization that could give an edge to the process and can make it a sustainable and financially competitive method of fuel and chemicals production.

Within the framework of this master thesis a liquid-liquid extraction experimental setup and a related procedure for the acquisition of liquid-liquid equilibrium (LLE) data were developed. Literature indicated Methyl Isobutyl Ketone (MIBK) as one of the most promising organic solvents for liquid-liquid extraction. The system that was studied in this frame was the ternary system, Water – Guaiacol –MIBK. The equilibrium experiments were performed in separating funnels under temperature regulation and both of the two distinct liquid phases (aqueous and organic) were withdrawn after equilibration for analysis. Gas Chromatography (GC) and Karl Fischer titration (KF) were used for the compositional analysis.

The experimental procedure resulted to be very good for attaining the goal of this master thesis and it presented some very interesting advantages. For example the use of separation funnels gave the opportunity to accurately measure the weight of the two liquid phases. Additionally, the use of KF gave an accurate analytical measurement for the water in the organic phase whereas most of the authors of similar works are using mass balance to calculate it.

Equilibrium data for the ternary system Water – Guaiacol – MIBK were successfully measured experimentally for the temperatures 30 and 55 °C under atmospheric pressure. Using the measured mass fractions, extraction yields, selectivities and distribution coefficients were measured to evaluate the extracting performance of MIBK. The extraction yields for the single stage extraction procedure applied in this work were up to 96%, depending on the relative amount of solvent to the feed (S/F). The values of S/F ranged from 0.05 up to 1 and it was indicated that the optimum value would be between 0.1 and 0.25. In all accounts, the work performed showed that MIBK can effectively be used as an organic solvent for the extraction of guaiacol from water and the experimental procedure that was adopted can very satisfactorily work for the acquisition of experimental LLE data.

Preface

This is a 10th semester Master Thesis project which was written in the spring semester of 2016 by a student enrolled in the Oil and Gas Technology Master's programme at Aalborg University Esbjerg.

The Bibliography is found in the back of the report, on page 50. The references are enclosed in square brackets such as [X] and the sources are referred to, using numbers.

In this report the decimal number is represented by a dot.

After the Perspective, the appendix can be found. The appendix contains the detailed methodology used for the Gas Chromatography including the program used with the instrument and the preparation of standard solutions.

Acknowledgements

I would like to thank:

My supervisor, Marco Maschietti, for his critical and substantial support for matters both theoretical and practical in all levels of the realization of this master thesis.

The laboratory staff and especially Dorte Spangsmark for her assistance and insight in technical matters related to experimental work.

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Chapter 1

1. Introduction

In the previous century the abundance of cheap fossil fuel like coal and petroleum created a sustainable energy source. However, this dependence on fossil fuel seems to act negatively in the sustainable growth of human society and economy. Mainly because of the definite need in reducing the greenhouse emissions and the constantly increasing demand on fuels [1]. In order to keep up with a sustainable industrial and economic growth, new sources of energy products had to be explored.

A lot of research has been conducted the last years on biomass as a promising source of a variety of energy related products including bio fuel and chemicals [2]. Different conversion processes are being studied in order to make biomass a more commercially viable raw material for the production of fuels and valuable chemicals. An important goal of research on the subject is to allow biomass to become a type of substitute to petroleum. This means that by processing the biomass, a wide variety of products may be produced. Similar to a conventional petroleum refinery the term biorefinery was introduced to define a combination of processes that can convert different biomass types to products equivalent to the ones that are derived from fossil oil [3]. The basic concept of the biorefinery is shown in Figure 1.1.

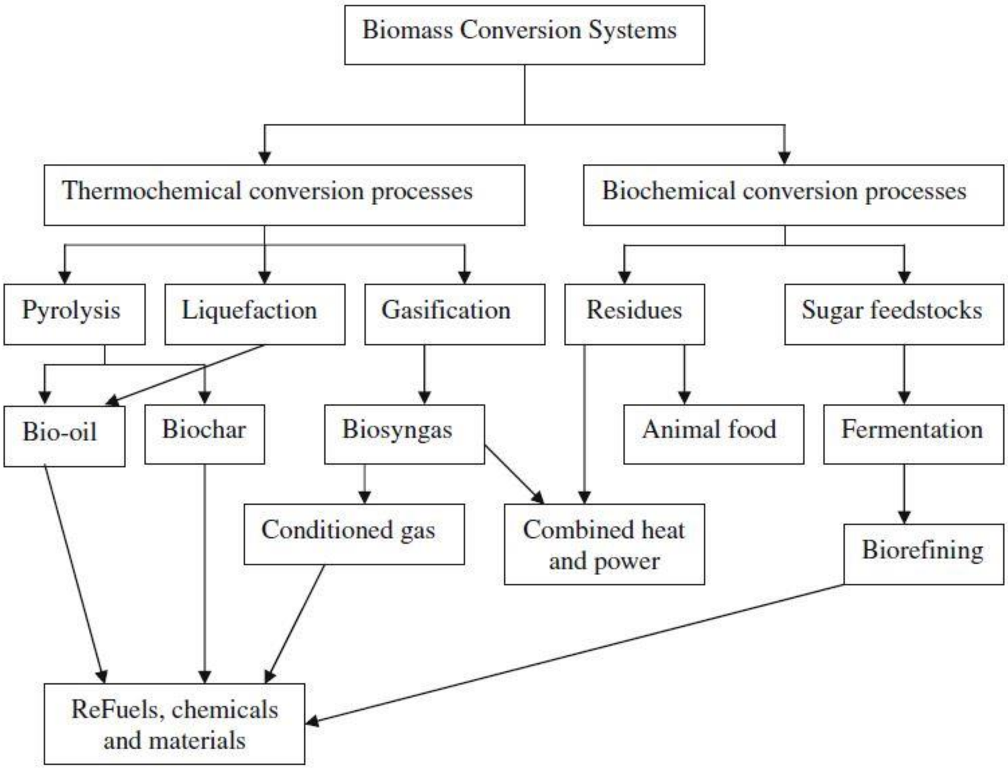

Figure 1.1: The general concept of Biorefinery [3]

Biomass has the advantage to be a “bio-renewable” raw material for the production of transportation fuel and a wide variety of chemicals [4]. Some of the technologies that are used in the petroleum refineries could be shared with the biorefineries. Although a substantial amount of research has to be performed for the many processing technologies that are needed for biomass conversion. This is crucial since the initial biomass source can be very different, from wood to municipal waste.

Additionally, biomass derived fuel is at the moment more expensive than petroleum but there seems to be prospect of creating value by the production of chemicals during the process. Those chemicals can be environmentally friendly additives for perfume, pesticide and other industries. Another utilization of bio fuel could be the mixing with conventional fuel in order to gradually reduce the amount of fossil oil that is being burned for energy [2].

There are a few important reasons why research is carried out on biomass conversion to a source of energy related products. Firstly it can be sustainable source. Biomass is renewable and also the utilization of the products has low environmental footprint (e.g. minimal greenhouse gas emissions) [5]. Another reason is that the last decade showed that the oil price can be unstable which makes planning of resources and production difficult. When oil demand is high and fossil oil supply is decreasing the utilization of biomass can be a viable way to substitute the lost supply. Additionally, petroleum production is only in control of a few countries and this creates a great political and financial inequality which had led from minor corporate corruption to wars between nations.

In general, biomass consists of different constituents. For example carbohydrates (e.g. starch), lignin or fats and proteins [5]. The characteristics of biomass vary a lot in accordance to the source. The source can be plants, waste of crops, cattle or municipal waste. The utilization of such sources of biomass can reduce the need of waste disposal which is detrimental to the environment [5]. The resulting biomass conversion products are dependent on the source of the biomass and also on the transformation process (liquid, gas or solid).

Lignin is considered one of the most interesting biomass resources that can be processed in order to produce bio fuel and chemicals, like phenolics [6]. Lignin is a complex organic chemical structure existing in woods [7]. It is a co-product of the paper pulping industry and currently a part of it is burned in order to generate energy. This practice has a lot of disadvantages like the increased emissions and that the produced energy cannot be stored easily [8]. Many different processes for the conversion of lignin into fuel and chemicals are being studied. Some of them are pyrolysis, hydrothermal conversion, electrochemical degradation enzymatic or catalysed degradation and others [8].

The hydrothermal processes have become important in chemical conversion because of the unique properties of water as a solvent. Furthermore, water is a benign component in regard of environmental implications [9]. This report is focused on the products of the hydrothermal conversion of lignin. In this process, compressed water at high temperatures is utilized as a reaction medium [10]. The chemicals that are produced by lignin conversion together with the bio fuel can add value which makes their recovery very important for the overall feasibility of the process.

1.1. Lignin

Lignin is a component that exists in all plants. After cellulose it is the second most abundant natural organic polymer on earth [11]. The name lignin defines the polymer located in the woody cell wall. It represents a 10-25 % of most of the plant based biomass. The structure of the molecule depends on the type of biomass and the recovery method. However the unifying chemical feature of lignin is a branched and cross-linked network polymer of phenylpropenyl units [7]. The three main monomers of which lignin is built of, are shown in Figure 1.2.

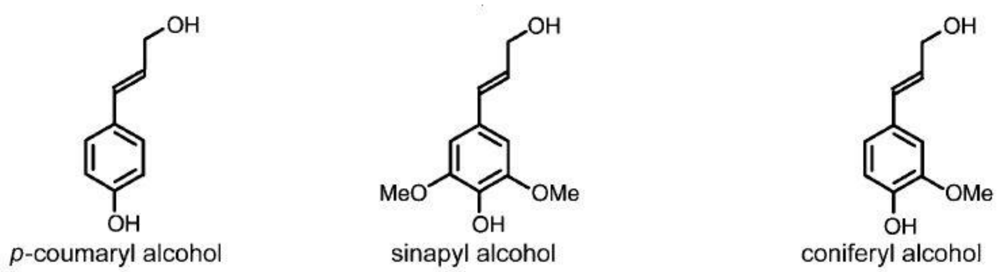

Figure 1.2: Major monomers of lignin [12]

Some important facts about lignin could be summarized in the following [7]:

- Large amounts available.
- Environmental concerns if disposed as waste.
- High energy content owing to the aromatic nuclei.
- Good adsorbent and ion exchange and adhesive properties.
- A direct source of various kinds of phenolic and aromatic compounds.

As it was previously mentioned, this project is interested in the phenolics that can be recovered from the transformation of lignin to bio oil.

1.2. Hydrothermal Conversion of Lignin

Hydrothermal processes are defined as chemical and physical transformations in water at elevated pressure and temperature. Typical conditions are 200-600 °C of temperature and 5-40 MPa pressure [13]. This process has the advantage that wet materials do not need to get dried and also that water is used as the reaction medium. This temperature suffices to initiate pyrolysis of the lignin biopolymers and the high pressure keeps the water in liquid phase [14].

Hydrothermal processing can be separated to three processes that depend on the actual conditions of pressure and temperature. For temperature lower than 200 °C the process is called hydrothermal carbonization and the product is a hydrochar which can be compared with low rank coal [14]. At temperatures between 200 and 370 °C, the process is called hydrothermal liquefaction and the product is liquid fuel (biocrude) [13]. Biocrude resembles petroleum and can be upgraded to the same range of fuel products. At temperatures above 370 °C the process becomes a hydrothermal gasification which produces a synthetic fuel gas [13]. In Figure 1.3 the phase diagram of water is shown. The regions of gasification and liquefaction are reported in the relevant temperature and pressure areas.

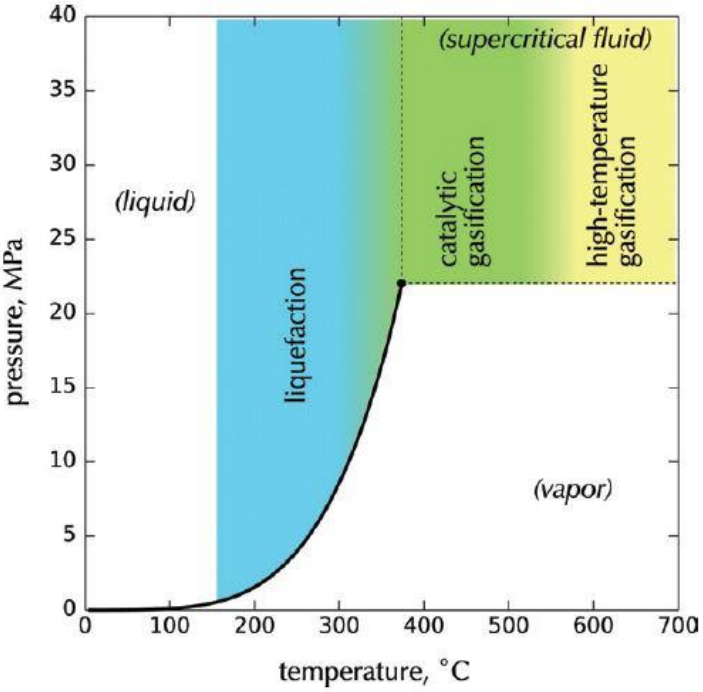

Figure 1.3: Phase diagram of water. Regions of liquefaction and gasification [13]

This report is focused on one of the streams generated during the liquefaction process, which is an aqueous stream. A simplified flow diagram of the process is shown in Figure 1.4. The figure is an adapted generalization found on literature [15] in which the main process blocks and streams are depicted. In this figure it is important to observe that a water stream out of the reactor can be treated and recirculated to a previous stage of the process. The treatment that is suggested in this case would be the liquid-liquid extraction (indicated by the dashed blue rectangle) which would add value to the process and also allow the water to be reused in a continuous way.

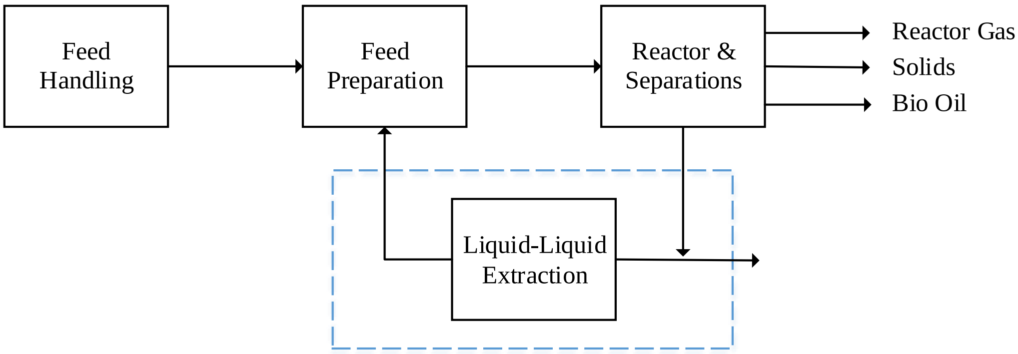

Figure 1.4: Hydrothermal Conversion block diagram with proposed liquid-liquid extraction process of the aqueous stream

The aqueous stream is interesting because it contains valuable chemicals and particular interest is put on the phenolic components that exist in it. These components are very important for numerous industries and also are considered high tier pollutants for water that is to be introduced to the ecosystem. Among them there can be cresols, catechol, guaiacol and others [8].

The phenolics that are used in industry are typically derived from phenol. Phenol was originally recovered from coal but nowadays more than 95% is industrially synthesized by oxidization of cumene, which is a product of crude oil [16]. The worldwide production of phenol was approximately 20 million tons per year in 2010 with the demand at the same levels [16]. Considering that lignin is a renewable feedstock coupled with the fact that by hydrothermal conversion it can provide phenolic components, the study extracting those from one of the process streams makes for a reasonable research goal. The current production of lignin is approximately 100 million tons per year and only 2% is isolated to be used for other purposes than burning for energy [17]. In the case that a larger amount of lignin was dedicated for the production of bio-oil, it could have the potential to become a large part of the production of valuable chemicals like phenol.

To highlight the importance of phenolics for the chemical industry, a number of applications can be mentioned as examples. Catechol is used as a raw material for many applications. In its pure form, it is used in photographic developers but it is mostly used through the form of its derivatives like guaiacol [18]. Guaiacol has a very strong flavor that makes it an important chemical for the perfume and food industry. Other guaiacol derivatives are used in medicine as expectorants, hemostatics, antiinfectives and in a lot more drug production processes. An additional use of catechol is as an agricultural chemical to produce insecticides [18].

The other important family of phenolics, which is met in the aqueous stream of lignin conversion, is cresol. Cresol is an important raw material that was originally obtained by coal tar. Since the 1960s cresol is another petrochemical derivative[19]. Cresol derivatives are being used as herbicides and insecticides and also as polymerization inhibitors (eg. distillation of styrene). Another important application of cresol is the production of resins that are used for structural and sealing material. The bactericidal properties make cresols also useful as disinfectants in soap [19]. The chemical structures of the above mentioned phenolics are shown in Figure 1.5.

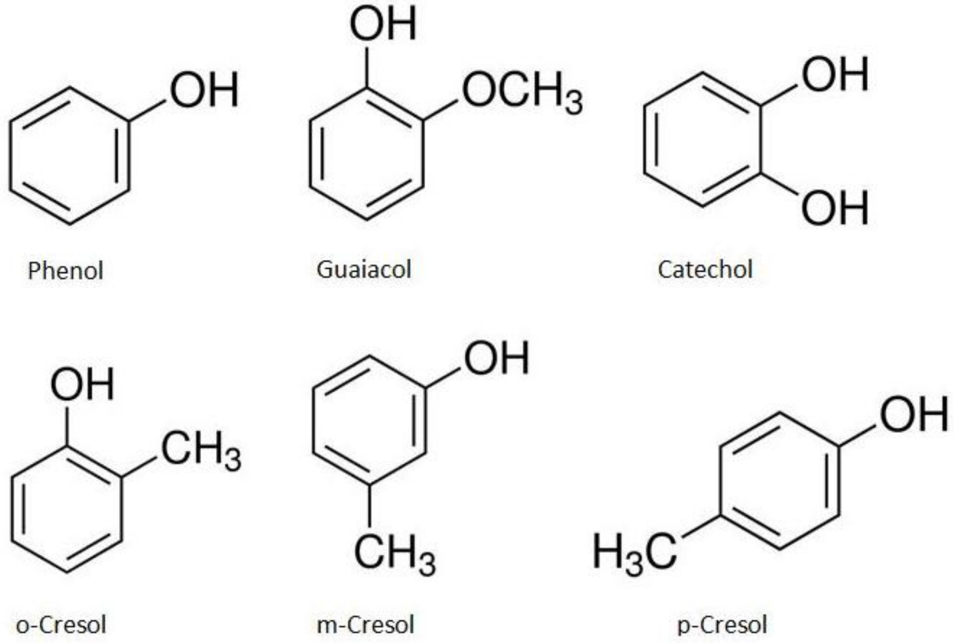

Figure 1.5: Chemical structure of phenol and phenolics

The fact that the aqueous phase of the conversion of lignin contains these phenolics makes it interesting for recovery methods to be studied. Additionally, as it is shown in Figure 1.4, the process entails recirculation of water which makes it necessary to remove the phenolics.

Liquid-Liquid extraction by using an organic solvent is being studied for the separation of phenolics from water. In the past, several studies have been performed on ternary systems that contain water, phenolics and an organic solvent in order to accumulate equilibrium data on these systems and evaluate different solvents. The initiative of this project was to study such a system, for which there are no experimental data and may be useful in the modeling of the industrial process of hydrothermal conversion of lignin. Liquid-liquid equilibrium data for ternary water-phenolic-solvent systems is one of the first steps for modeling processes of multicomponent systems.

1.3. Recovery of Phenolics from the Aqueous Phase

Liquid-liquid extraction using organic solvents may be an effective way to remove pollutants from industrial aqueous phases. The same process can be very useful recovering chemicals that can be used in other industries [20]. The extraction in industrial level is typically done in columns in which the solvent and the feed are coming into contact. In Figure 1.6, a simplified process flow diagram (PFD) of a typical industrial level liquid-liquid extraction process is shown.

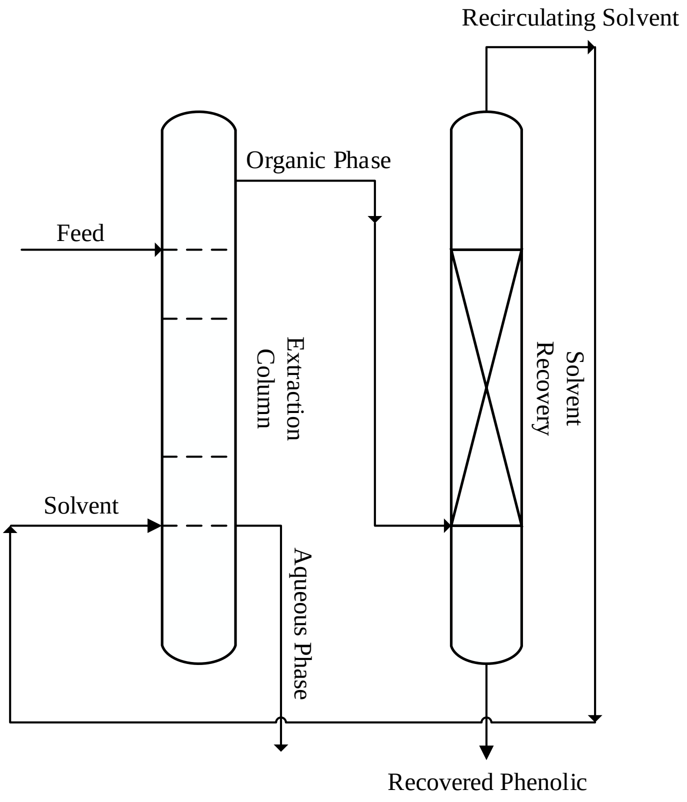

Figure 1.6: Process Flow Diagram (PFD) of typical industrial extraction process

Figure 1.6 represents the details of the liquid-liquid extraction block that is included inside the dashed blue line in the overall lignin hydrothermal conversion process block diagram of Figure 1.4. Systems like this normally include a distillation column to separate the high value components and the solvent which can then be reused for the continuous process of extraction.

Liquid-liquid extraction experiments on the perspective of such an industrial application can help the optimization of the process of extraction by finding for example optimal amounts of solvent or temperature. Additionally, the initial step of process design is constituted by the experimental study of binary or ternary sub-systems that combined can simulate the original process. The typical practice for the latter is to perform liquid-liquid equilibrium (LLE) experiments in order to acquire distribution coefficients of the phenolics in the aqueous and organic (solvent rich) phases respectively.

Literature indicates that polar organic solvents like ketones, ethers and esters are promising because of their property of hydrogen-bonding with phenolics but not with themselves [20]. Methyl isobutyl ketone (MIBK) is one of the most promising of these solvents for the recovery of phenolics from water [11–13]. The chemical structure of MIBK is shown in Figure 1.7. The electronegativity of the oxygen that is present in this molecule favors the creation of hydrogen bonding with the phenolic molecules that were shown in Figure 1.5. Additionally, the MIBK molecule does not have hydrogen connected to a highly electronegative atom, which deter the molecules of hydrogen bonding with themselves.

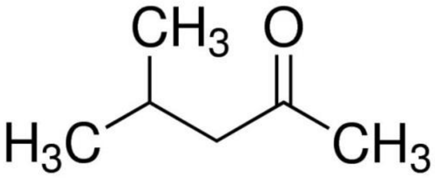

Figure 1.7: Chemical structure of Methyl Isobutyl Ketone

1.4. Literature Overview

The interest of this project falls in the study of ternary systems of water phenolics and MIBK. In the past, there has been research on the subject for some of the phenolics. At the extent of the knowledge of this work there are no experimental LLE data for guaiacol. The importance of the specific phenolic in the chemical industry was underlined in Section 1.2.

In Table 1.1 the main research papers on the subject are summarized in order to give an insight of what has been realized until now. This literature study was used as a guide to decide the planning some aspects of the present work. From this study some very important conclusions have been extracted and are reported as follows:

- MIBK is one of the most promising solvents for liquid-liquid extraction.
- The temperature have to be carefully controlled during liquid-liquid equilibrium experiments.
- Gas chromatography is a viable method to measure the concentration of organic components in both aqueous and organic phases.
- For most phenolic components that are derived from the hydrothermal conversion of lignin, there is a significant lack of equilibrium data. Especially for guaiacol there are no data, according to the extent of this literature research.

The above points were derived from studies on systems similar to the one that was planned in this project. These were systems of water, a phenolic component and an organic solvent. These indications were considered in order to decide the organic solvent to be used for this work and additionally the specific phenolic component that would be studied.

Table 1.1: Literature review

Paper	**Temp** (°C)	**System of Components**	**Analytical Instruments**
Narasimhan et al 1962 [21]	30 44.4	Water-Phenol-Butyl Acetate	GC-FID
Won and Prauznitz 1975 [20]	25 45	Water-Phenol-Butyl Acetate or MIBK or Isopropyl Ether	GC-FID
Greminger et al 1980 [22]	30 50 75	Water-Phenol-MIBK or Diisopropyl Ether	GC-FID
Chufen Yang et al 2007 [23]	25	Water-Phenol-Hydroquinone-MIBK	GC-FID
Yong Lei et al 2013 [24]	25 40 50	Water-Phenol-Methyl tert butyl ether	GC-FID
Yun Chen et al 2014 [25]	25 50	Water-Phenol-Hydroquinone-MBK	GC-FID
Zhuo Wang et al 2015 [26]	25 40	Water-Cresol (o-, m-, p-)-MIBK	GC-FID

* Where:
MIBK: Methyl Isobutyl Ketone, MBK: Methyl Butyl Ketone
GC-FID: Gas Chromatography-Flame Ionization Detector

With all the above considered, it seemed that liquid-liquid equilibrium data of aqueous systems containing phenolic components and MIBK could give an edge in simulation of industrial liquid-liquid extraction. Additionally, studies of equilibrium for such systems can give indications on the performance of MIBK and possibly other organic solvents on extracting the valuable phenolic components from water in numerous industrial applications.

1.5. Project Delimitation

In the current state of environmental awareness and instability of the petroleum industry, research about biomass derived fuels and chemicals, thrives. The object of this research is to create energy related products and valuable chemicals that can supplement the ones derived from petroleum and in some cases even substitute them. Different sources of biomass are being studied extensively and ways to optimise the utilization of the promising ones are being researched. Lignin being one of the most abundant biomasses coupled with the fact that its utilization until now is very limited makes it a good candidate for the above.

As in all modern processes, a large part of their viability rests with their effective modelling. Modelling is almost always based on data that are provided by experimental work on systems that simulate individual parts of the real process which when combined can create a complete and accurate prediction tool. One of these processes is the hydrothermal liquefaction of lignin. Water is used for this process as a reaction medium and it has been proved that during the conversion the water ends up to contain a considerable amount of phenolic components. In addition to the high value of the phenolics, the water needs to be reused continuously in a sustainable manner and therefore it has to be free of them. This fact makes extraction of phenolic components from water an important part of the process.

Liquid-liquid extraction has appeared as an effective process of recovering phenolics from water. The experimental data that are needed to simulate a liquid-liquid extraction process are typically equilibrium data for ternary systems that can be combined by using a thermodynamic model in order to simulate the original multicomponent system. Therefore in this project after literature research on existing experimental data it was observed that there are no data at all for one of the most valuable phenolics which is guaiacol. Additionally it was realized by the literature study that Methyl Isobutyl Ketone (MIBK) is one of the most promising organic solvents that can be used to extract phenolic components from water. In light of these discoveries, the present project was decided to focus on experimental work for the liquid-liquid equilibrium of the ternary system Water – Guaiacol – MIBK.

1.6. Project Definition

Based on the problem delimitation, the main focus of this project was:

Develop and utilize a laboratory scale liquid-liquid extraction method for Guaiacol by using Methyl Isobutyl Ketone (MIBK) as an organic solvent. The method should provide accurate experimental liquid-liquid equilibrium data for the ternary system Water-Guaiacol-MIBK.

The work performed for this project was the liquid-liquid equilibrium study of a ternary system for which no published experimental data exist. Such data for a number of ternary systems of water-MIBK and different phenolics are very important in order to enable the modelling of an industrial process. In this case the extraction of valuable phenolics from the aqueous stream that is recirculated during the hydrothermal conversion of lignin.

The experimental equilibrium data were obtained for two temperatures (30 and 55 °C) and the goals that were set in order to successfully acquire accurate data can be summarized as:

- Set a procedure of mixing the three components and settle the system adequate time to obtain equilibrium.
- Set an accurate procedure of separately withdrawing the two liquid phases from the separation funnels.
- Develop analytical measurement methods that are able to provide accurate compositional results for the two liquid phases.
- Analyse the data and compare with similar systems to assess the reliability of the experimental data.

Chapter 2

2. Experimental Procedure and Materials

2.1. Experimental Apparatus

The liquid-liquid equilibrium experiments took place in a controlled environment, using pure substances to create a synthetic solution. This solution was produced resembling the aqueous phase of the hydrothermal conversion of lignin, containing a phenolic that was to be recovered. The temperature was regulated by a heating immersion circulator in a water bath as shown in Figure 2.1. The model of the heating immersion circulator was a Julabo ED with a heating capacity of $2\,kW$ and a recirculating pump with a flow rate capacity of $15\,\frac{L}{min}$. The manufacturer states in the specification sheet that this model is appropriate for water baths up to $50\,liters$. The water bath was a mgw LAUDA model with operating dimensions of $49\,cm\,x\,30\,cm\,x\,20\,cm$ (30 liters). Additionally, the surface of the water was filled with insulating material in order to limit heat loss.

Figure 2.1: Temperature regulating water bath

The experiments for this project were performed at two temperatures, 30 and 55 degrees Celsius (°C). The lower temperature was chosen in order to always be above the ambient temperature which would ensure that it can be regulated by the heater. The higher temperature was chosen after a few experimental runs at 45 °C that showed no significant differences compared to similar runs at 30 °C.

For both temperature levels, several measurements were taken inside separation funnels filled with water. Ensuring that the funnels were covering different space in the water bath the temperature was measured and showed that it was stable within a limit of ±0.1 °C.

The separation funnels that were used for the experiments were either 100 or 250 ml depending on the convenience of the material that had to be contained in them. The two types are shown in Figure 2.2.

Figure 2.2: Separation funnels (250 and 100 ml)

2.2. Chemicals

In order to create a solution that could simulate the water generated by the hydrothermal conversion of lignin, an aqueous stock solution was produced. The model component that was used was pure natural guaiacol. The organic solvent for the extraction process was methyl isobutyl ketone (MIBK) since literature suggested that it has better extraction yield than other solvents and also create less implications [20], [22]. In this section the chemical and physical properties of the chemicals that were used in this project are stated.

Throughout the experiments, distilled water was used. The water that was distilled originated from purified water by reverse osmosis. The quality of the distilled water was not measured but the manufacturer of the distillation apparatus reports that it produces water with a conductivity value lower than 2.3 micro Siemens per cm $\left(\frac{\mu S}{cm}\right)$ at ambient temperature [27] which ensures a high quality of water.

The chemicals that were used for this work, including the ones used for analytical measurements are reported in Table 2.1. In this table the supplier information and the purity of the chemicals is reported.

Table 2.1: Suppliers and purity of chemicals used in this work

Component	**Supplier**	**Assay**	**Product No.**
Methyl Isobutyl Ketone	Sigma Aldrich	≥98.5%	360511
Guaiacol	Sigma Aldrich	≥99.0%	W253200
Bromobenzene (IS)	Merck Millipore	≥99.0%	8017861000
Methyl Ethyl Ketone (IS)	VWR	≥99.0%	25654.292
n-propanol (IS)	VWR	≥99.0%	20858.293

* The chemicals noted as IS were used as internal standards for Gas Chromatography.

Table 2.2: Chemical and physical properties of Methyl Isobutyl Ketone and Guaiacol

Component	**MIBK**	**Guaiacol**
CAS no.	108-10-1	90-05-1
Formula	$C_6H_{12}O$	$C_7H_8O_2$
Molecular weight	$100.16\ \frac{g}{mol}$	$124.14\ \frac{g}{mol}$
Description	Colorless liquid	Colorless oily liquid
Density @ 25 °C	$0.801\ \frac{g}{ml}$	$1.129\ \frac{g}{ml}$
Solubility @ 25 °C in water	$17.39\ \frac{g}{L}$ [28]	$23.33\ \frac{g}{L}$ [28]
Solubility @ 25 °C of water in	$1.90\ \frac{g}{L}$ [29]	-
Boiling point	117 °C	202 °C
P_{sat} @ 25 °C	$2.20\ kPa$	$0.0133\ kPa$
pK_a	9.93 [30]	25 [31]

In Table 2.2, the physical and chemical properties of the two components that were used in this project for the liquid-liquid extraction experiments are reported. All information was taken from the manufacturer specification sheet except if another literature source is stated. The values that were stated by the manufacturer were also cross checked in literature and were found in good agreement.

2.3. Preparation of stock solution

A stock solution (feed) that could simulate the water generated by the hydrothermal conversion of lignin was produced for the extent of the experiments. The stock was an aqueous solution of guaiacol in distilled water. The general procedure can be described as follows:

- An appropriate volumetric flask was mounted on a micro balance and was tared.
- The desired amount of guaiacol was charged in the volumetric flask and the balance was tared again after the exact weight of the phenolic was taken.
- The volumetric flask was then filled with distilled water and the weight of the added water was measured on the balance.
- A magnetic stirrer was inserted in the flask, which was then sealed with a cap and mounted on a magnetic stirring engine.
- Stirring took place for 1 hour to ensure the complete dissolution of the phenolic and the visible homogeneity of the solution.
- The stock solution was stored in a cabinet protected from light until usage.

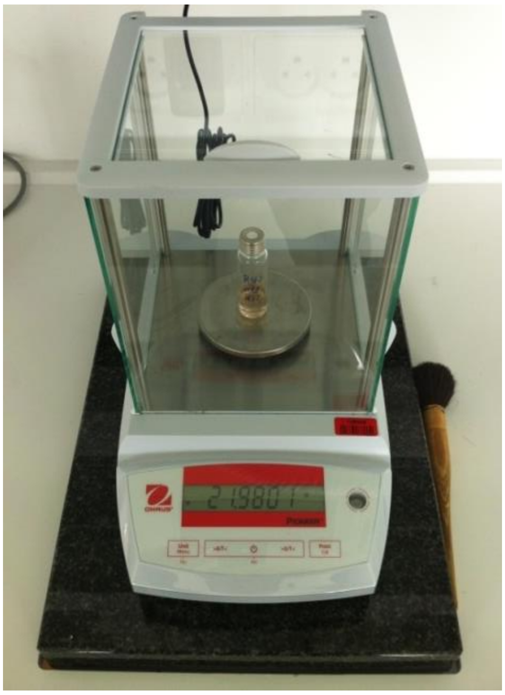

Figure 2.3: OHAUS Pioneer analytical balance

The production of the stock solution was performed in ambient conditions. The amount of stock solution prepared never exceeded 1 kg, which was used in a span of a few days. All weight measurements for this project were performed on an OHAUS Pioneer (PA214C) analytical balance with readability of four decimal digits (0.0000), which is shown in Figure 2.3.

2.4. Liquid-Liquid extraction

Since the goal of this project was to study the extraction of phenolic components from an aqueous stream, using an organic solvent, several extraction experiments were performed with varying the process conditions and analyzing the resulting liquid-liquid equilibrium. These conditions were the temperature and the composition by varying the solvent to feed ratio (S/F).

The general description of the procedure can be reduced to the following points:

- An amount of feed solution was weighted according to the S/F ratio of each experimental run.
- The appropriate amount of MIBK was afterwards weighted in a sealed container to avoid vaporization losses. After mounting and taring the glass container on the balance, with a syringe the appropriate amount of MIBK was weighted.
- The two substances were charged in a separation funnel and the containers were back weighted to account for losses during the transfer.
- Each funnel was shaken vigorously three times for 3 minutes.
- Between the shaking the funnels would remain in the water bath in order for the system to reach the chosen process temperature.
- Finally the funnels were positioned in the water bath and the system left to settle for 2 h.

The above mentioned procedure was applied for both temperature levels on which the experiments were performed. However there were a few details that changed in the procedure for the higher temperature. These changes were the result of observations made after a number of preliminary experiments at elevated temperature (e.g. 45 and 55 °C). The modifications in the procedure were as follows:

- After the feed and the solvent were in the funnels, the latter were positioned inside the water bath to achieve the desired temperature before the shaking procedure took place (typically 20-30 minutes).
- All weight measurements were performed in sealed containers because the evaporation losses could potentially be higher due to the elevated temperature.
- The organic samples that were collected for analysis purposes were diluted with pure MIBK in order to avoid possible demixing at ambient temperature.

Inspired by literature, it was assumed that 2 hours is enough time for the equilibrium to take place [20]. Additionally, some preliminary experimental runs were performed in order to study how settling time was influencing the extraction yield. Experiments at the same conditions and varying settling time from 2 to 24 hours showed that the system would reach a stable equilibrium state after 2 hours of settling.

In this project the mixing of the stock solution with the solvent was performed by manual shaking. The procedure was inspired by literature [32] and after the performance of some preliminary experiments with a variation of shaking time it was decided that repeating a 3 minute vigorous manual shaking was enough for the mixing of the components.

After the settling time, two liquid phases with a well-defined interphase existed in the separating funnel. On the top the lighter organic phase (MIBK rich), and on the bottom the heavier aqueous phase. The general procedure for the withdrawal of the two phases from the separating funnels can be described by the following:

- From the top of the funnel, an appropriate amount (typically 3-8 ml) of the organic phase was retrieved carefully using a syringe. The mass of the sample was measured and the sample was stored in a closed glass container for analytical measurements.
- An appropriate amount of the aqueous phase (typically 15-25 ml) was afterwards extracted from the bottom of the funnel. The mass of the sample was measured and it was sealed and stored in a glass container for analytical measurements
- The remaining aqueous phase was conveyed in a beaker and the mass was measured. This part of the aqueous phase was disposed after it was weighted.
- The remaining organic phase was discharged from the bottom of the funnel in a beaker in order to be weighted and then disposed.

By weighting the two liquid phases, the overall mass balance between their sum and the feed-solvent sum was calculated for each individual run. The average discrepancy was -0.7% which was reckoned reasonable considering evaporation and small amounts of remaining material in the funnel during the procedure. In general this discrepancy remained under -1% and only in a few cases of extractions at 55 °C it reached as high as -1.5% which was assumed reasonable since the evaporation can be higher at that temperature.

The use of separation funnels had the advantage of allowing the retrieval of the two phases separately with a reasonably high accuracy. This enabled the weighting of the phases in order to find an accurate relative weight ratio. This ratio is the phase fraction (α) and it is defined as the ratio of the aqueous phase mass divided by the overall mass of the two extracted phases:

$$\alpha = \frac{m_{aq}}{m_{aq} + m_{org}} \quad [2.1]$$

Where:

- α : Phase fraction $\left(\frac{g}{g}\right)$
- m_{aq} : Mass of aqueous phase at equilibrium (g)
- m_{org} : Mass of organic phase at equilibrium (g)

The equilibrium experiments were performed in a thermostatic bath at a predefined temperature. After the equilibrium was ensured, the funnels were removed from the water bath and mounted on clamps to withdraw the two phases. In Figure 2.4 a separation funnel mounted on the clamps is shown with a magnified view of the interphase between organic and aqueous phase. The sampling procedure of the two phases took place relatively quickly in a range of a few minutes. Therefore the system at equilibrium temperature was expected not to be disturbed at the few moments of the sampling procedure.

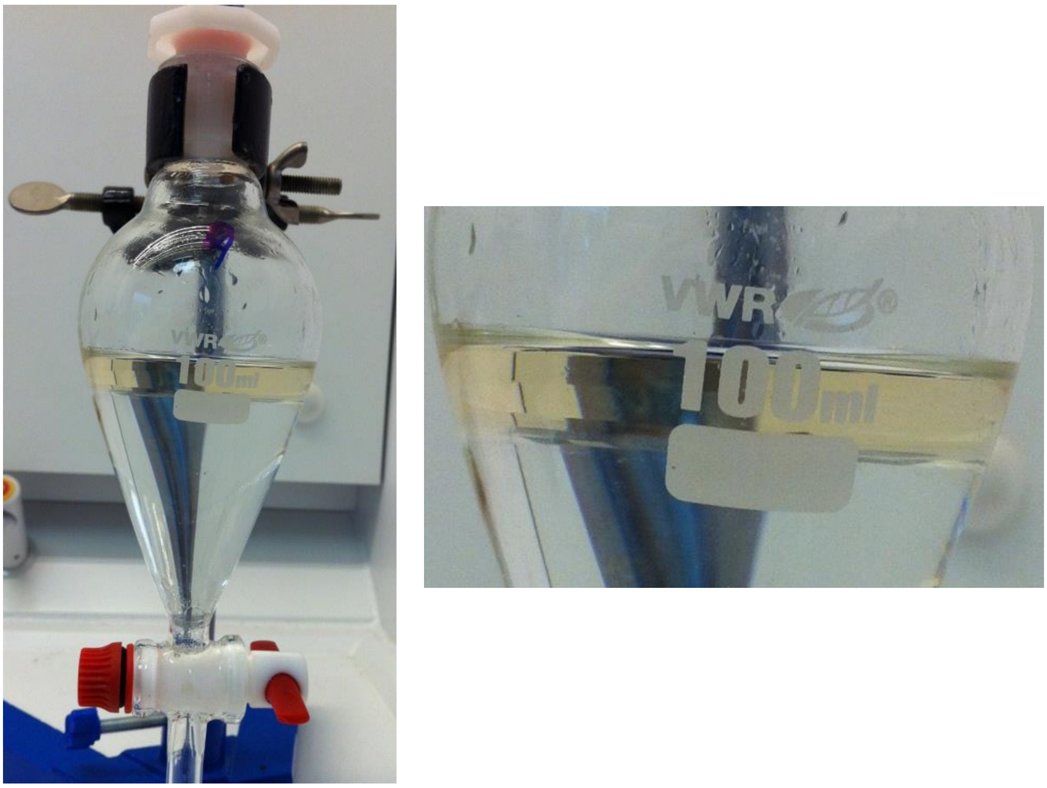

Figure 2.4: Separation funnel in which the two phases have a well-defined interphase

2.5. Analytical Methods

2.5.1. Gas Chromatography

Gas chromatography (GC) is an analytical measurement procedure that involves the volatilization of an injected mixture sample followed by the separation of the different components in a chromatographic column. One important rule for GC to be applicable is that components (analytes) that are going to be measured have to be able to vaporize without decomposing [33]. A carrier gas is used for the transfer of the components from the injection device (injector) to the column. In the case of the instrument that was used for this project the carrier gas was helium. The principle of determination in GC applications is the distribution of the components between the mobile phase (carrier gas) and a stationary phase that exists in the column. The timing of elution of a component is what determines the separation and that makes possible for a detector to quantify the components in the mobile phase after elution. In Figure 2.5, a simple figure of a gas chromatograph is presented.

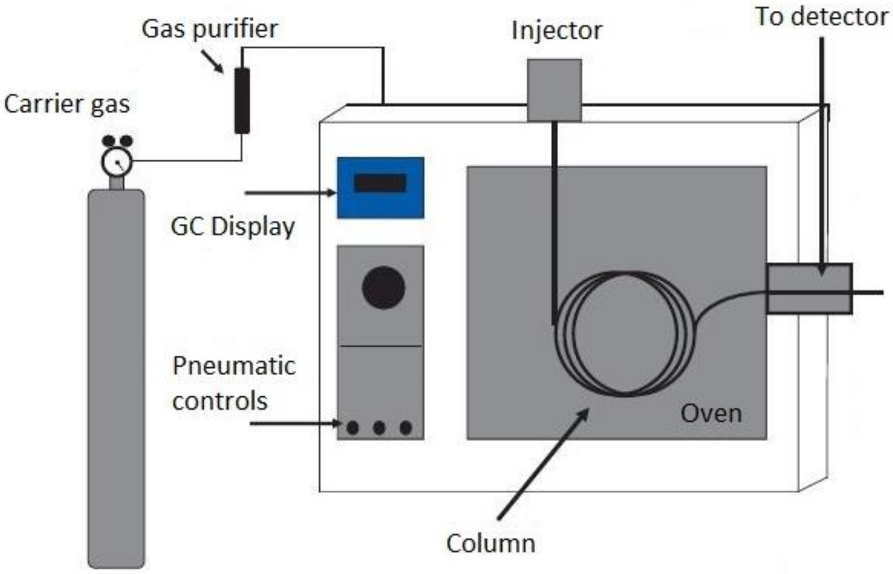

Figure 2.5: Schematic representation of GC [33]

The separation of the components takes place inside the heated column that contains the stationary phase. The components move with the carrier gas and they are selectively retarded by the stationary phase. As the temperature of the oven is increasing the components that are retained by the stationary phase are successfully released to the mobile phase depending on their boiling point [33]. Each component then is led to the detector in order to be quantified.

Detectors are specially designed for gas chromatography and some of them are thermal conductivity (TCD), flame ionization (FID) or a more complex mass spectrometer (MS) [33]. For this project a GC-FID configuration was used to quantitate the organic components in the aqueous and organic phases. More specifically a Perkin Elmer Clarus 500 gas chromatograph was used with a Perkin Elmer BAC-1 Advantage column (Inner diameter: 0.32 mm, Length: 30 m, Film thickness: 1.80 μm). The configuration that was used for the analytical measurements in the present work is available in Appendix I. The FID is one of the most commonly used detectors for hydrocarbon characterization [33] and as it was observed in section 1.3 it is the detector that is typically used for analysis of ternary systems containing water, phenolics and organic solvents.

The detector uses a combination of hydrogen and air which are burned. The flame burns the analytes that elute the column and produce ions which create a current flow. That current flow is what provides a signal that is used to quantitate the components of the mixture that is being analyzed [33]. The use of a gas mobile phase dictates that the analytes are volatile in order to separate between the two phases [34]. Additionally, since the analysis is based on burning the analytes, it follows that water is a component that cannot be quantitated by the GC-FID. In Figure 2.6, a cross section of a typical FID detector is shown.

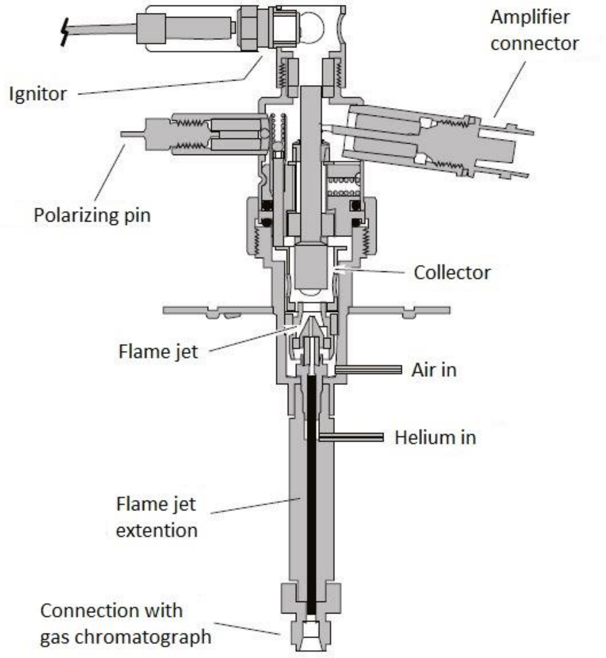

Figure 2.6: Flame ionization detector cross section [35]

Each liquid-liquid extraction experiment produced an organic and an aqueous liquid phase which both were analyzed by the GC to acquire the concentration $\left(\frac{g}{L}\right)$ of the guaiacol in the organic phase and both guaiacol and MIBK in the aqueous phase. In order to smooth the potential error of the gas chromatography measurements, every sample of unknown concentration was analyzed in triplicates and the average value was taken. The average absolute deviation was no higher than the following values:

- 0.010 $\frac{g}{L}$ for guaiacol in the organic phase.
- 0.016 $\frac{g}{L}$ for MIBK in the aqueous phase.
- 0.040 $\frac{g}{L}$ for guaiacol in the aqueous phase.

The GC was separately calibrated for each of the two phases, every time a batch of samples was accumulated. A combination of the external and internal standard methods was used for the calibration of the instrument and the measurements.

The calibration of the gas chromatograph is referring to a procedure that is performed prior the quantitation of samples with unknown concentrations. That typically includes measurement of samples with a known concentration and using the GC response of those in order to compare to the response of the samples to be analyzed. The samples with the known analyte concentrations are the standard solutions and that is how they will be referred to from here onwards. Details about the preparation of the standard solutions are available in Appendix I.

The success of the calibration depends on accuracy factors like the accuracy in the preparation of the standard solutions and the reproducibility of the same measurement conditions. The accuracy of the standard solution preparation was ensured by the use of volumetric flasks with high accuracy (A class) of $\pm 0.01\, ml$ up to $\pm 0.1\, ml$ depending on the overall size of the flask which ranged from $5\, ml$ up to $100\, ml$. For smaller quantities a precision pipette was used. More specifically, the Gilson Microman M100 $(10 - 100\, \mu l)$ and M1000 $(100 - 1000\, \mu l)$ were used, along with a positive displacement tip in order to accurately sample small amounts of the liquid chemicals that were used in this project.

The additional factor, on which the analyte quantitation accuracy depends on, is the amount of sample that is analyzed after an injection in the GC. There are two important conditions that affect this and these are the split ratio, and the overall amount that is injected by the automatic sampler (injector) of the GC. Only a part of the amount injected reaches the column and the remaining of the injection is vented (split). Accordingly, the split ratio (SR) is defined as [33] :

$$\mathrm{SR} = \frac{\text{Column Flow} + \text{Vent Flow}}{\text{Column Flow}} \qquad [2.2]$$

Typical split ratios range between 10:1 to 400:1 [33]. The split ratio is regulated by the instrument after the operators programming and is intended to be constant throughout repeated injections of the same sample. This fact makes the amount that the automated sampler injects, the only factor that can change the amount which is entering the column. GC injectors may not be completely accurate in consecutive injections and that is the reason why in this project internal standards (IS) were used for the analysis along with the external standard calibration. This basically means that an external standard calibration was used where additionally, in each injection of an unknown sample (or standard), a constant amount of the internal standard ensured that imperfections in the injected amount were compensated.

The external standard calibration method utilizes the comparison of the analytical response of a component that is to be quantitated and that of the same component in the standard solutions. The response in the case of the FID detector that was used in this project is the area of a peak. An example of a GC result is reported in Figure 2.7, in which the response in form of peaks is shown for guaiacol as the analyte and bromobenzene as the IS.

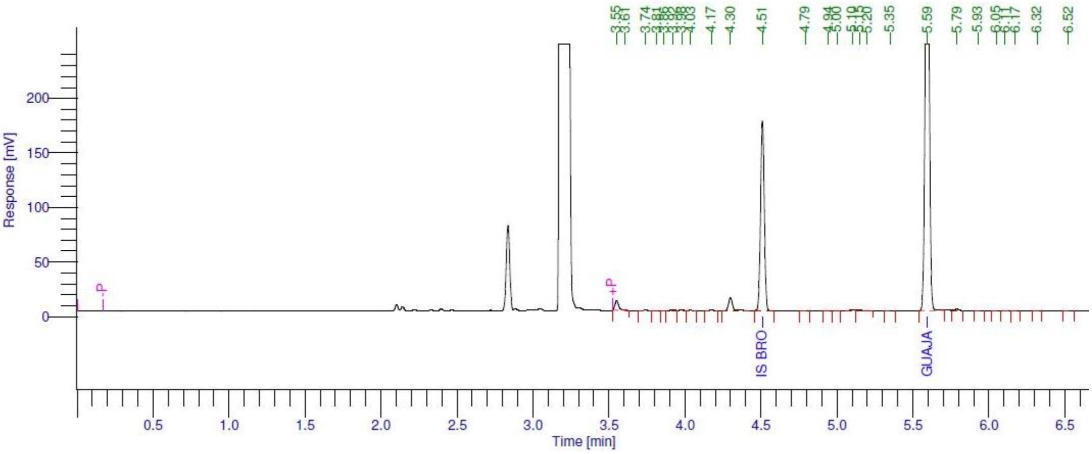

Figure 2.7: Gas chromatograph response example

The standard solutions were prepared by dissolving known amounts of pure analyte in the same solvent which was present in the samples to be quantitated (MIBK). During the preparation of the standards the chosen internal standard was added in the same amount for all the standard solutions. The analytical response (peak areas) of these standards provides a calibration curve for the analyte. In certain concentrations this curve can be linear. Under this condition the response is proportional to the concentration of the analyte.

In the case that the response is linear the calibration curve would follow the relation:

$$y = a \cdot x + b \quad [2.3]$$

In this case y would be the peak area of the analytical response and x the concentration of the analyte. Under the assumption that the intercept (b) is very small it can be omitted. This practically means that in the absence of analyte from a measurement, there would be no response. Under these assumptions and introducing convenient symbols equation 2.3 can be rewritten:

$$\mathrm{A_{an}} = \mathrm{RF_{an}} \cdot \mathrm{C_{an}} \quad [2.4]$$

Where:

- $\mathrm{A_{an}}$: Peak area of analyte
- $\mathrm{RF_{an}}$: Factor of proportionality of analyte (response factor)
- $\mathrm{C_{an}}$: Concentration of the analyte

If equation 2.4 is solved for C_{an} the concentrations of analyte would be:

$$C_{an} = \frac{A_{an}}{RF_{an}} \quad [2.5]$$

Additionally, the concentration of the IS is always constant between measurements and therefore the response factor (RF_{IS}) can be introduced in a similar way and solved for the concentration of the IS:

$$C_{IS} = \frac{A_{IS}}{RF_{IS}} \quad [2.6]$$

Where:

- C_{IS} : Concentration of IS in injected sample
- A_{IS} : Peak area of internal standard

The ratio of the concentration of the analyte and the concentration of the IS would therefore be given by:

$$\frac{C_{an}}{C_{IS}} = \frac{\left(\frac{A_{an}}{A_{IS}}\right)}{\left(\frac{RF_{an}}{RF_{IS}}\right)} \quad [2.7]$$

In order to add the IS correction of the injected amount the relative response factor of the analyte (RRF) can be introduced and defined as:

$$RRF = \frac{\mathrm{RF_{an}}}{RF_{IS}} \quad [2.8]$$

Solving equation 2.7 for the concentration of the analyte and substituting with equation 2.8:

$$C_{an} = C_{IS} \cdot \frac{\left(\frac{A_{an}}{A_{IS}}\right)}{RRF} \quad [2.9]$$

In this way the internal standard method is combined with the external standard in order to compensate for inaccuracies of the injection system of the gas chromatograph. This is possible due to the fact that the injection inaccuracy affects the response of the analyte in the exact same way as it affects the response of the IS and that mutual effect is calculated by the RRF.

As it can be observed by equation 2.4 the units of the response factors and areas are not relevant since they cancel each other and therefore they are not reported. The compositional results of the GC analysis in this project were calculated in concentration units $\left(\frac{g}{L}\right)$. However the results were conveniently converted to mass fractions as they are more useful for reporting equilibrium data. This conversion was performed by using the experimentally measured density (ρ) of each phase as follows:

$$w = \frac{\frac{C}{1000}}{\rho} \quad [2.10]$$

Where:

- w : Mass fraction of component $\left(\frac{g}{g}\right)$
- C : Analytical measured concentration of the component $\left(\frac{g}{L}\right)$
- ρ : Experimental density of liquid phase $\left(\frac{g}{ml}\right)$

The density of the phases was measured experimentally by the weighting of small volume samples on the analytical balance. The accuracy of the volume samples was ensured by the use of the precision pipette with the same tip for all measurements. The additional measure taken to improve the precision of this procedure was the calibration of the pipette with distilled water. The calibration was performed by measuring the mass of several samples of distilled water. Afterwards, the room temperature was measured and the accurate density of water was acquired from the National Institute of Standards and Technology (NIST) to be used to calculate the real volume that the specific pipette configuration was sampling.

Since the method of quantitation was explained above, examples and typical values for the method can be reported. An example of a calibration curve using the combination of the external and internal standards is shown in Figure 2.8. The x-axis represent the ratio between the analyte concentration and the IS concentration, whereas the y-axis represents the ratio between the peak area of the analyte and the IS. Each level of the line represents triplicate injections of the standard solutions. In the example of Figure 2.8, the linearity is displayed by the value of the coefficient of determination (R^2), which the closer it is to 1 the higher the linearity is.

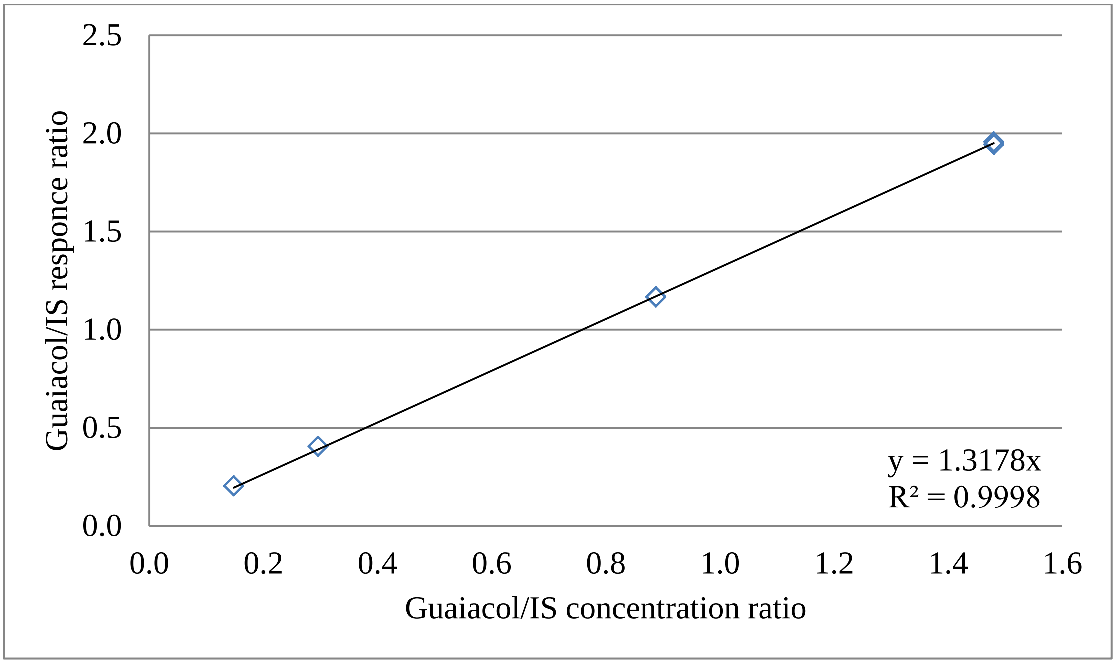

Figure 2.8: Calibration curve example for guaiacol in the organic phase

New calibrations where performed often in order to ensure that the gas chromatograph performed at the same level of accuracy. The typical R^2 values for the calibrations in this project were approximately 0.999 for the organic phase similar to the example of Figure 2.8. In the case of the aqueous phase the linearity was somewhat lower as in the example shown in Figure 2.9.

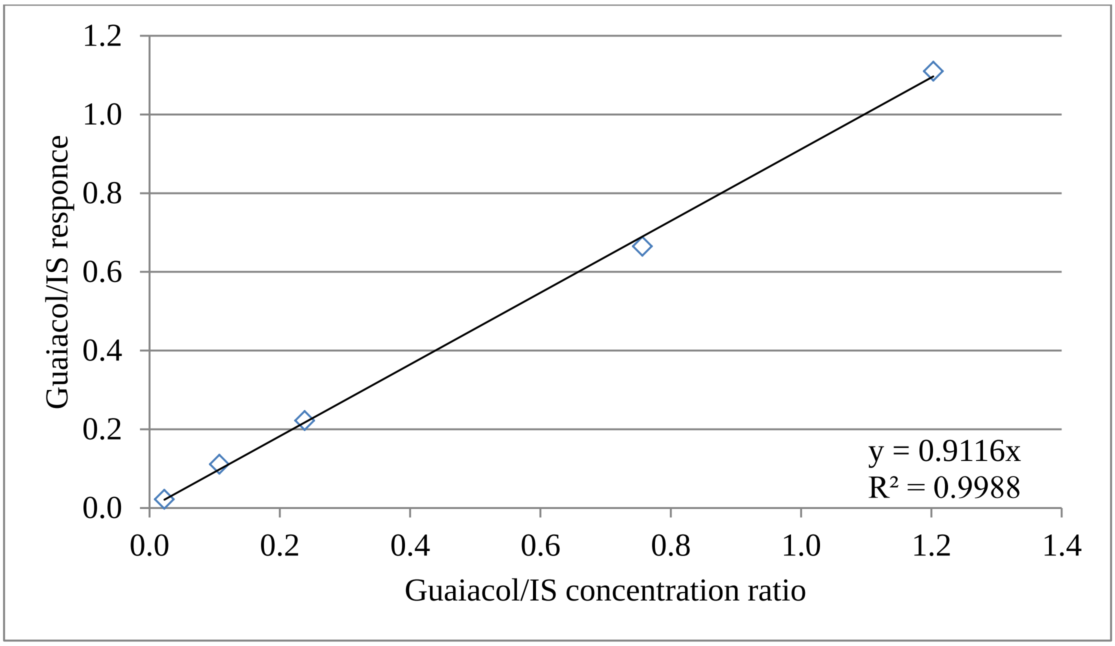

Figure 2.9: Calibration curve for Guaiacol in the aqueous phase

There was an apparent difficulty to get linearity values of above 0.999 for the aqueous phase. However whenever that was the case it was ensured that the relative difference between the values calculated by the regression line and the experimental value of the standards were not higher than ±3 %. In addition, the reproducibility of the results for triplicate injections of the standards was controlled before a calibration was used for unknown samples. When continuous measurements of a large amount of samples were programmed to be analysed, one or more of the standards were measured in between to ensure that the response results did not drift more than an acceptable level (e.g. 2% of the initial response).

A linear calibration curve that is acquired by the external standard method represents only a narrow range of analyte concentrations. The samples that were to be analyzed had unknown concentrations that sometimes would fall outside of that linear range. For that reason, it was necessary that some of the samples should be further diluted with pure solvent (MIBK or distilled water). This dilution was performed accordingly, in order to reach an analyte concentration inside the calibration limits and give an analytical result that is reasonable. This procedure was performed depending on the expectation of analyte concentration or in some cases after a GC measurement that gave quantitative results outside of the linear range.

In the aqueous phase the concentration of the two components was sometimes very different with MIBK being as higher as 40 times than the concentration of guaiacol. Each component had its own calibration and the linear range could not be achieved for both of them in a single injection. That was compensated by performing one injection for the guaiacol measurement and a second one with a more diluted sample for the measurement of MIBK.

2.5.2. Karl Fischer Titration

Karl Fischer titration (KF) is a well-established method of determining the water content in an organic phase. The method is able to measure both dissolved and suspended water with high accuracy in a wide range of concentrations [36]. Typically the accuracy of KF is approximately 1% of the available water and the concentration ranges from 100 % down to 0.01% [37].

The method that was used for this project is a volumetric method in which water is participating in a reaction with sulfuric dioxide and iodine in a methanolic solution. A base is used as a buffer for the reaction. Fischer used pyridine as a base in his initial experiment but later it was discovered that any appropriate base (RN) can be used [36]. The components that are used nowadays are less toxic than pyridine.

The reaction equation can be represented as follows:

$$H_2O + I_2 + [RNH]^+ \, SO_3CH_3^- + 2RN \longrightarrow [RNH]^+ SO_4CH_3^- + 2[RNH]^+ I^- \qquad [2.11]$$

The determination of the water content is done by measuring the amount of iodine that is consumed. For example, in the case of a methanolic solvent the consumption ratio of I_2 is 1:1 with H_2O. This ratio is what allows the titration instrument to give an accurate value of the water content in a sample injected to the titration vessel.

There are different solutions (titrants) that are used to determine that ratio. These solutions are chosen, mainly according to the expected concentration of water in the organic mixture that is going to be measured. Additionally, the amount of titrant (volume) that is used for a known concentration of water has to be determined in order for the titration to be successful for samples of unknown concentration. This determination is typically done with a standard solution and it is called titer determination.

In the case of this project the titer was determined by using a standard solution of 1% water content. The titer was expected to always be approximately $2\,ml$ of titrant for $1\,mg$ water as it is suggested by the manufacturer of the titrant. The titer determination took place every few days to ensure that air humidity did not cause any drift in the measurements.

The solvent, the titrant and the water standard that were used for the KF in this project are reported in Table 2.3.

Table 2.3: Chemicals used for the Karl Fischer Titration

Purpose	**Supplier**	**Commercial Name**	**Product No.**
Water Standard	Sigma Aldrich	HYDRANAL-Water Standard 10.0	34849
Titrant	Sigma Aldrich	HYDRANAL-Titrant 2	34811
Solvent	Sigma Aldrich	HYDRANAL-Solvent	34800

In order to evaluate the compatibility of MIBK with the KF procedure and the chemicals that were available, a number of test measurements were performed. Standard solutions of MIBK containing up to 1.33% water were prepared and the KF results showed a deviation no more than 0.1% of the expected amount of water. Additionally, the tests showed that the titration vessel had to be emptied and filled with fresh solvent once every approximately 6-10 injections. This is typical for KF but for some ketones like MIBK it is required more often.

In Figure 2.10, the titration instrument that was used for this project is shown. Karl Fischer titrations were performed at least in triplicates for each of the extraction samples with an average absolute deviation no higher than 2 %.

Figure 2.10: Metrohm 870 KF Titrino plus

Chapter 3

3. Results and Discussion

This project was inspired by the extraction of phenolics from an aqueous stream that is present during the hydrothermal conversion of lignin to biofuel. This is an innovative process on a multicomponent system. As with all processes modelling is a very good way to optimize the operating conditions. One of the initial requirements that enable the modelling is experiments from which equilibrium data can be obtained. Typically this is done by studying simpler systems of components (e.g. binary, ternary). Since this project was focused on the aqueous phase of the process, and given the time frame, a specific ternary system was chosen to be studied. In the following sections the results of the experiments that took place in this work and their significance are being discussed.

3.1. Water-Guaiacol-MIBK

The significance of guaiacol for the chemical industry, the lack of published experimental data and the fact that it is one of the most abundant phenolics present during the hydrothermal conversion of lignin, led it to be the main component for the liquid liquid extraction experiments for this project. The experiments took place for the ternary system of Water (1) – Guaiacol (2) – Methyl Isobutyl Ketone (MIBK) (3). The aim of the experiments was mainly the acquisition of liquid-liquid equilibrium (LLE) data for the said system. Additionally, the performance of MIBK as an extraction medium was studied.

The study of the ternary system was performed by varying the equilibrium temperature and also the overall initial composition of the mixture. The latter was accomplished by changing the solvent to feed ratio for given feed stock solutions between experimental runs:

$$S/F = \frac{m_{solvent}}{m_{feed}} \quad [3.1]$$

Where:

- S/F : Solvent to feed ratio
- $m_{solvent}$: Mass of pure MIBK
- m_{feed} : Mass of stock solution (Water + Guaiacol)

The summary of the conditions that were varied during the experiments are reported in Table 3.1. In this table the target values are reported and as expected the experimental values could have a small difference than the nominal values. Additionally, the number of experimental runs at each condition set is reported. The conditions on which a lot of repetitions were performed (e.g 30 °C, 1 wt% stock, 0.25 S/F) were conditions on which reproducibility or condition effects (e.g. settling time, shaking procedure) were tested.

Table 3.1: Experimental conditions for the Water – Guaiacol – MIBK ternary system

Temperature (°C)	**Stock Solution Composition** (wt% Guaiacol)	**S/F** $\left(\frac{g}{g}\right)$	**Repetitions**
30	1	1	2
		0.5	3
		0.25	8
		0.1	4
		0.08	1
		0.05	1
	2	0.1	1
		0.08	1
		0.05	1
55	1	0.5	1
		0.25	1
		0.1	2
		0.05	2
	2	0.25	1
		0.1	2
		0.08	1
		0.05	2
Total number of experimental runs			37

The stock solutions that were produced for the experiments had a difference from the target value no higher than $0.026\,\%$. In the experimental runs the S/F ratio varied reasonably, no more than $0.13\,\%$ of the target value. The temperature was stable inside the separation funnels at the target value $(\pm 0.1\ °C)$.

The two extracted liquid phases in this report are going to be noted by a unique subscript as follows:

- a : Aqueous phase
- b : Organic phase

Additionally the three components will be characterized by a unique numeric subscript:

- 1 : Water
- 2 : Guaiacol
- 3 : MIBK

The results of the LLE experiments are presented later in this chapter, in the form of plots and ternary diagrams. In all figures the compositional data are reported as the mass fractions of each of the components in each phase or percentages of those. The mass fractions are defined as:

$$w = \frac{m_c}{m_{ph}} \quad [3.2]$$

Where:

- w : Mass fraction of component (g/g)
- m_c : Mass of component in the specific phase (g)
- m_{ph} : Overall mass of the phase (g)

The mass of the phases is the experimental value that was measured with the analytical balance after the withdrawal of the two phases from the separating funnels.

The mass fraction of guaiacol in the organic phase was calculated from the GC analysis by equation 2.10. The mass fraction of water in the organic phase was calculated by the Karl Fischer titration as mentioned in section 2.5.2. The mass fraction of MIBK in the organic phase was the subtraction of the mass fractions of guaiacol and water from 1.

For the aqueous phase, both guaiacol and MIBK mass fractions were calculated by equation 2.10. The mass fraction of water was then calculated as the subtraction of the mass fractions of guaiacol and MIBK from 1.

For each experimental run the overall mass balance and the individual mass balances for the components were calculated. That was done in order to support the accuracy of the experimental procedure. The overall mass balance was calculated as:

$$MB_{tot} = \frac{(m_a + m_b) - (m_{feed} + m_{solvent})}{m_{feed} + m_{solvent}} \cdot 100 \quad [3.3]$$

Where:

- MB_{tot} : Overall mass balance (%)
- m_a : Mass of aqueous phase (g)
- m_b : Mass of organic phase (g)

The mass balance for each component was calculated as:

$$MB_{component} = \frac{(m_{c,a} + m_{c,b} - m_{c,in})}{m_{c,in}} \cdot 100 \quad [3.4]$$

Where:

- $MB_{component}$: Mass balance of component
- $m_{c,a}$: Mass of component in aqueous phase (g)
- $m_{c,b}$: Mass of component in organic phase (g)
- $m_{c,in}$: Overall mass of component in the mixture (g)

As it was mentioned in section 2.4 the overall mass balance value calculated by equation 3.3 was no higher than 1.5 % with an average of 0.7 %. In the case of individual mass balances as they were calculated by equation 3.4, discrepancies of ±3% were observed in the majority of the experimental runs. These were deemed acceptable taking into account evaporation losses or small inaccuracies of the analytical measurements. In cases that the discrepancies exceeded this limit, the compositional analysis of the phases was repeated with GC calibrations in a narrower range. In most cases the results of the reanalysis gave lower discrepancies and therefore replaced the initial values.

In order to evaluate the ability of MIBK to extract guaiacol from an aqueous solution the extraction yield was defined as:

$$Y = \frac{m_{2,b}}{m_{2,total}} \cdot 100 \quad [3.5]$$

Where:

- Y : Extraction yield percentage
- $m_{2,b}$: mass of guaiacol in organic phase (g)
- $m_{2,total}$: mass of guaiacol in feed (g)

Additionally the distribution coefficient of guaiacol was calculated as an additional measure of the capability of MIBK to extract guaiacol from the aqueous phase. The distribution coefficient is defined as:

$$D = \frac{w_{2,b}}{w_{2,a}} \quad [3.6]$$

Where:

- D : Distribution coefficient of guaiacol
- $w_{2,b}$: Mass fraction of guaiacol in the organic phase
- $w_{2,a}$: Mass fraction of guaiacol in the aqueous phase

The selectivity is another factor that measures the ability of the solvent to extract the solute (guaiacol) from the aqueous phase and it is defined as:

$$S = \frac{\left(\frac{w_{2,b}}{w_{1,b}}\right)}{\left(\frac{w_{2,a}}{w_{1,a}}\right)} \qquad [3.7]$$

Where:

- S : Selectivity of the solvent (MIBK) to the solute (guaiacol)
- $w_{1,b}$: Mass fraction of water in the organic phase
- $w_{1,a}$: Mass fraction of water in the aqueous phase

In the following sections the LLE experimental data were used to evaluate the performance of MIBK in liquid-liquid extraction. Additionally the data were discussed in a qualitative manner in order to extract significant results.

3.1.1. Performance of MIBK as an Extraction Agent

In this subsection the extraction yields the distribution coefficients and the selectivities were used as indicators for the general behaviour of the extraction of guaiacol from the aqueous phase by MIBK. The extraction yield can be used as a technical tool in order to understand the effect of the amount of solvent to its ability to extract the solute. In Figure 3.1 and Figure 3.2 the extraction yield is plotted against the solvent to feed ratio for different conditions.

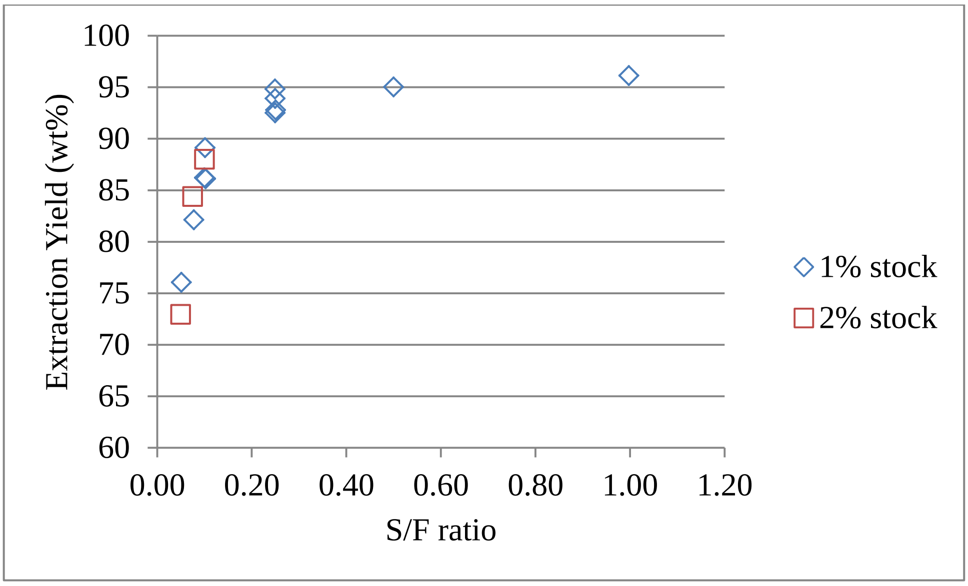

Figure 3.1: Extraction yield of guaiacol with MIBK at 30 °C

Figure 3.1 shows the extraction yield for the experiments that were performed at 30 °C**.** The first observation of these results is that the higher the amount of solvent the more guaiacol is extracted which was according to expectations. However, it can be observed that for S/F 0.5 and 1, the yield of the extraction is increasing only approximately 5% compared to 0.25. This fact could suggest that a compromise of S/F ratio and extraction yield could be the case, at a value lower than 0.5.

A compromise on the amount of solvent used would be reasonable for example if the solvent usage cost was higher of what could be gained by the extracted guaiacol. Since in an industrial extraction process MIBK is supposed to be reused like it was shown in Figure 1.6 these costs could pertain to a number of sources. For example these could be the purchasing of make up MIBK for inevitable losses and the energy that is needed for the recovery. Both of those costs depend mainly on the total amount of MIBK that is being used. With these considerations, an increase of 50 or 100% to the amount of solvent used for a 5% increase in the extraction yield might not seem reasonable.

Figure 3.2 shows the extraction yield results for the experiments that were performed at 55 °C. Similarly to the results at 30 °C the higher the amount of MIBK the higher the extraction is. Also the small increase of extraction yield between S/F 0.5 and 0.25 verify the observation that it may not be economical to increase the S/F more than 0.5.

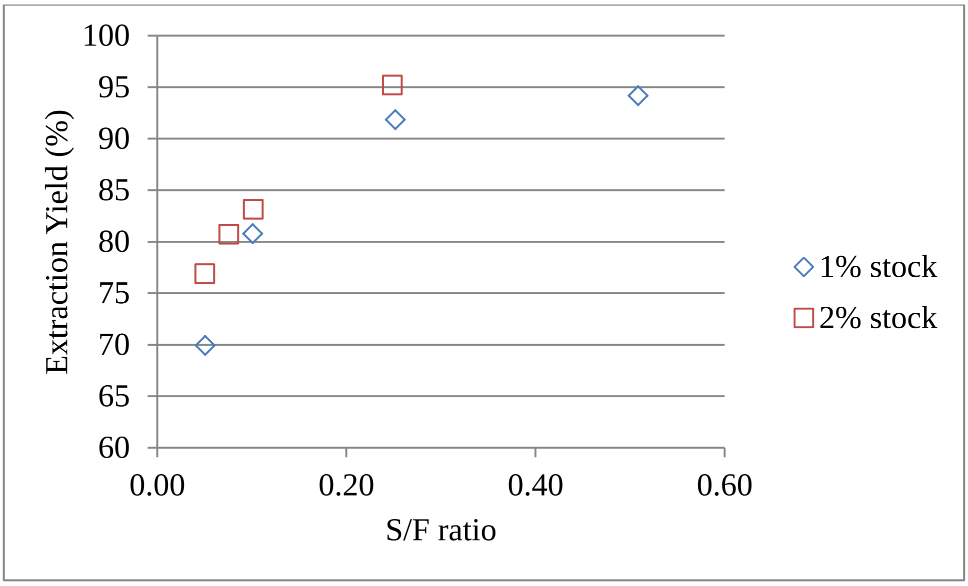

Figure 3.2: Extraction yield of guaiacol with MIBK at 55 °C

Another interesting comparison for the present system was the distribution of guaiacol between the two phases and the temperature effect on that distribution. In Figure 3.3 the mass fraction of guaiacol in the aqueous phase is plotted against the mass fraction of guaiacol in the organic phase at the two temperatures that were studied.

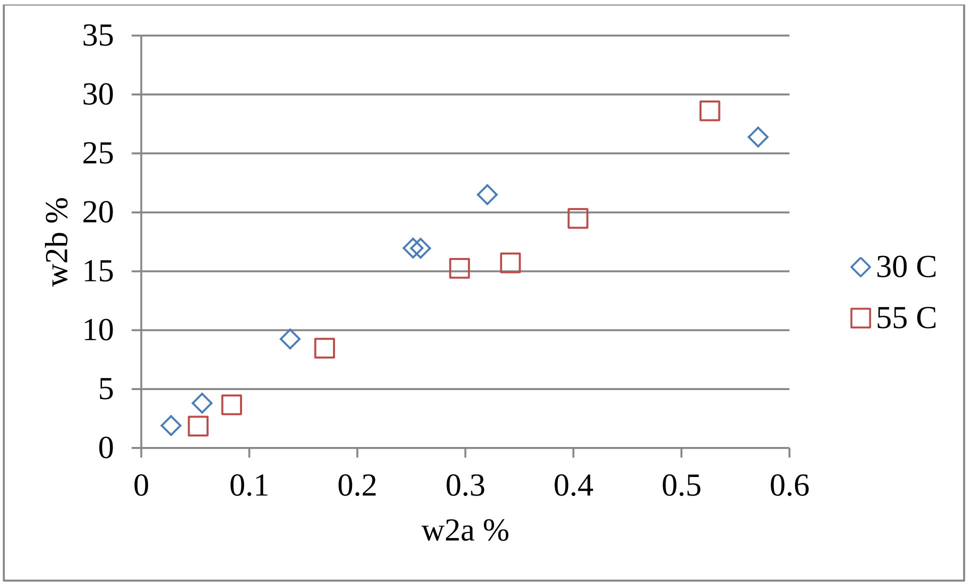

Figure 3.3: Distribution of Guaiacol in the aqueous (a) and organic (b) phase at 30 and 55 °C

From Figure 3.3 it may be observed that for the higher temperature the mass fraction of guaiacol has a tendency to be higher in the aqueous phase for a given mass fraction in the organic phase compared to the lower temperature. That seems to be the case for overall guaiacol mass fractions 0.8% to 1.86%.

The opposite seems to happen for the highest guaiacol overall composition (1.90 wt%) which could mean that for higher guaiacol content the higher temperature is more effective during the extraction. For the lower guaiacol overall mass fractions the temperature does not seem to have an effect on the distribution. The last two observations could serve only as guides for further study because they are not definitive since they could own to analytical measurement inaccuracies.

Regarding the absolute value of the distribution coefficient, it seems that compared to the extraction of phenol with MIBK, the extraction of guaiacol is more difficult. The typical distribution coefficients that are reported in literature [20], [22], [23] for phenol are over 100 and the results of this work show the highest value being a little over 70. Taking into account other phenolic molecules the literature reports distribution coefficients for cresols (o-, p-, m-) much higher with values up to 385 [20], [26]. However these can only be loosely compared with the current work because in one case [20] the author reports only one value and the other [25] is using Methyl Butyl Ketone as a solvent. The only molecule that according to literature has a much lower value of distribution coefficient is catechol with values reported up to 20 [20].

One of the factors that affect the distribution is the solubility the phenolics in water. It is expected that molecules with higher solubility like catechol (~ 461.4 $\frac{g}{L}$ @ 30 °C) [28] would be more difficult to extract than cresols (~ 22 $\frac{g}{L}$ @ 30 °C) [28] that have lower solubility in water. And that seems to be the case according to literature for cresols and catechol. In addition, the solubility of phenol falls higher than cresol and much lower than catechol (~ 84 $\frac{g}{L}$ @ 30 °C) [28] . It seems that the extraction ability of MIBK for those molecules follow the trend that as the solubility of the molecule in water is increasing the distribution coefficient decreases. However, in case of guaiacol, that its solubility is close to the one of cresol, the distribution coefficient that was found in this work is much lower than the one reported for cresol. That could leave the space of trying a different solvent for the case of extracting guaiacol and also the study of other factors that can affect the distribution.

Considering the selectivity of the extraction process a comparison between the two temperatures could give some interesting indications. In Figure 3.4 the selectivity was plotted against an increasing overall guaiacol mass fraction for the two temperatures that were studied. From this diagram a few general observations could be made. Initially the selectivity seems to start from lower values for the higher temperature which may indicate that the extraction would be more successful at the lower temperature. This could add to the similar observation for the distribution of guaiacol between the two phases.

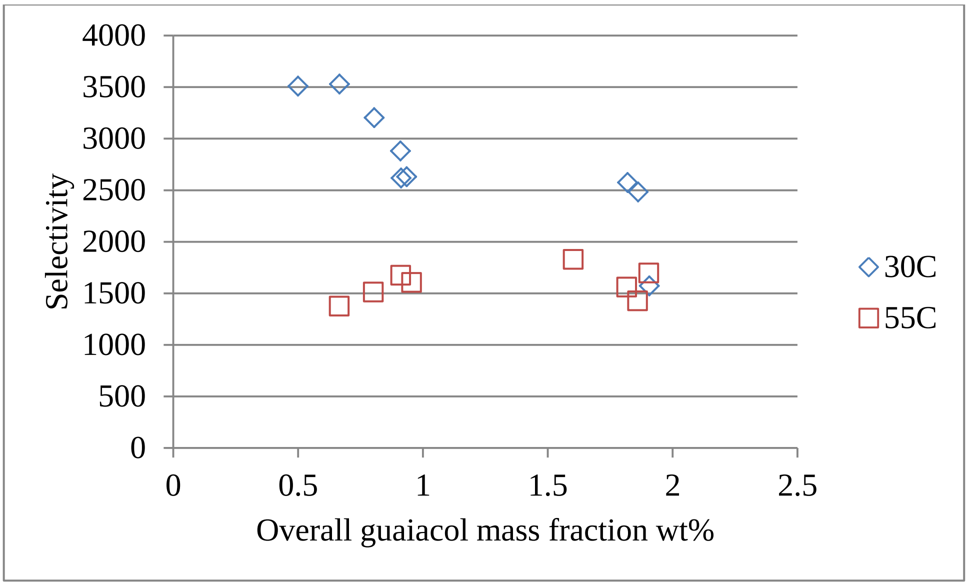

Figure 3.4: Selectivity comparison between 30 and 55 °C for different overall mass fractions of guaiacol

In this figure something that could be considered is that there seems to be a trend of the selectivity to decrease as the mass fraction of guaiacol increases for the lower temperature. That is reasonable since the increasing of initial guaiacol is performed by increasing the stock feed and decreasing MIBK which leaves a lower amount of MIBK to extract a higher amount of guaiacol and therefore the mass fraction of guaiacol in the aqueous phase is higher.

3.1.2. Phase Equilibrium Behaviour

The phase behaviour of the system that was studied was plotted in ternary diagrams for the two temperatures that were studied. The ternary diagrams can give an overall idea of how the composition of the two phases is changing in the ternary system. In these diagrams the three apexes represent a composition in which only one of the components exists in pure form. In this case the left apex represents water, the right MIBK and the top guaiacol. The tie lines that were produced in these ternary diagrams are the connection of the ternary composition of the aqueous phase (left side) and that of the organic phase (right side).

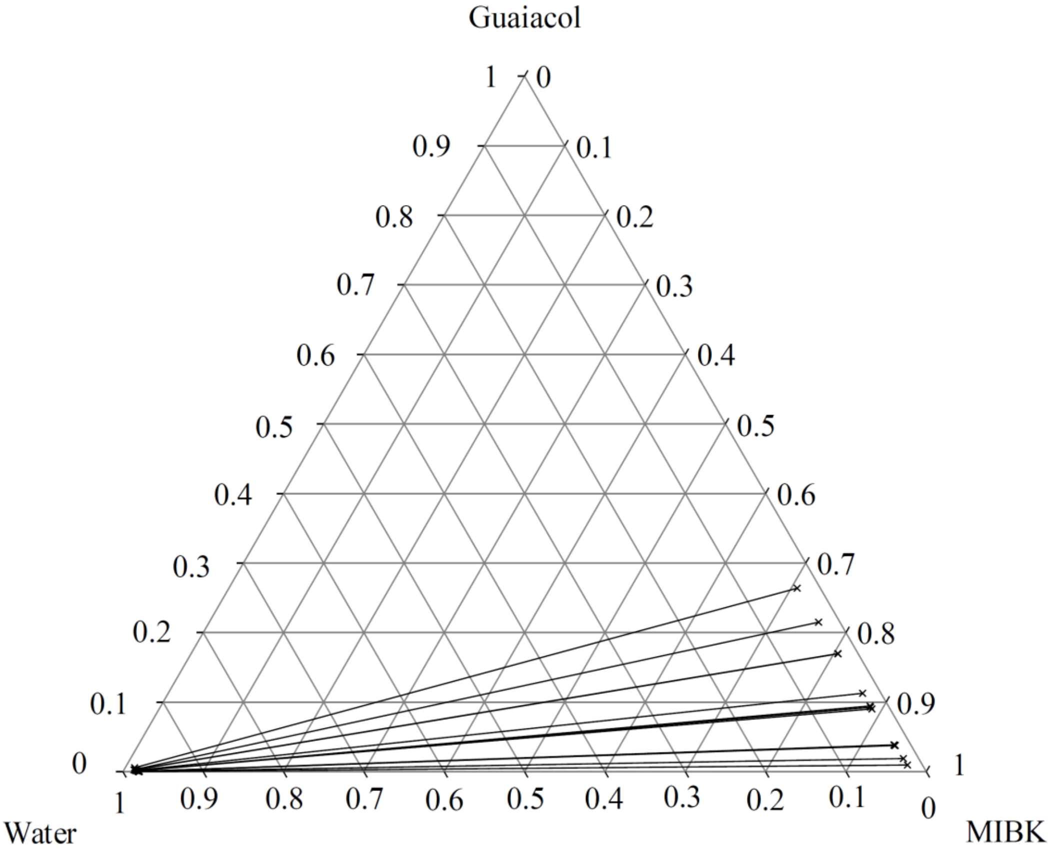

Figure 3.5: Ternary diagram of mass fractions for the system Water – Guaiacol – MIBK at 30 °C

In these ternary diagrams it is observed that the effect of temperature for the equilibrium values is not very high. In both cases the aqueous phase retains a relatively stable composition. For the organic phase the results show that the mass fraction of water starts from a little higher value for the 55 °C but except for that the value increases only a little as the mass fraction of guaiacol is increasing in the organic phase.

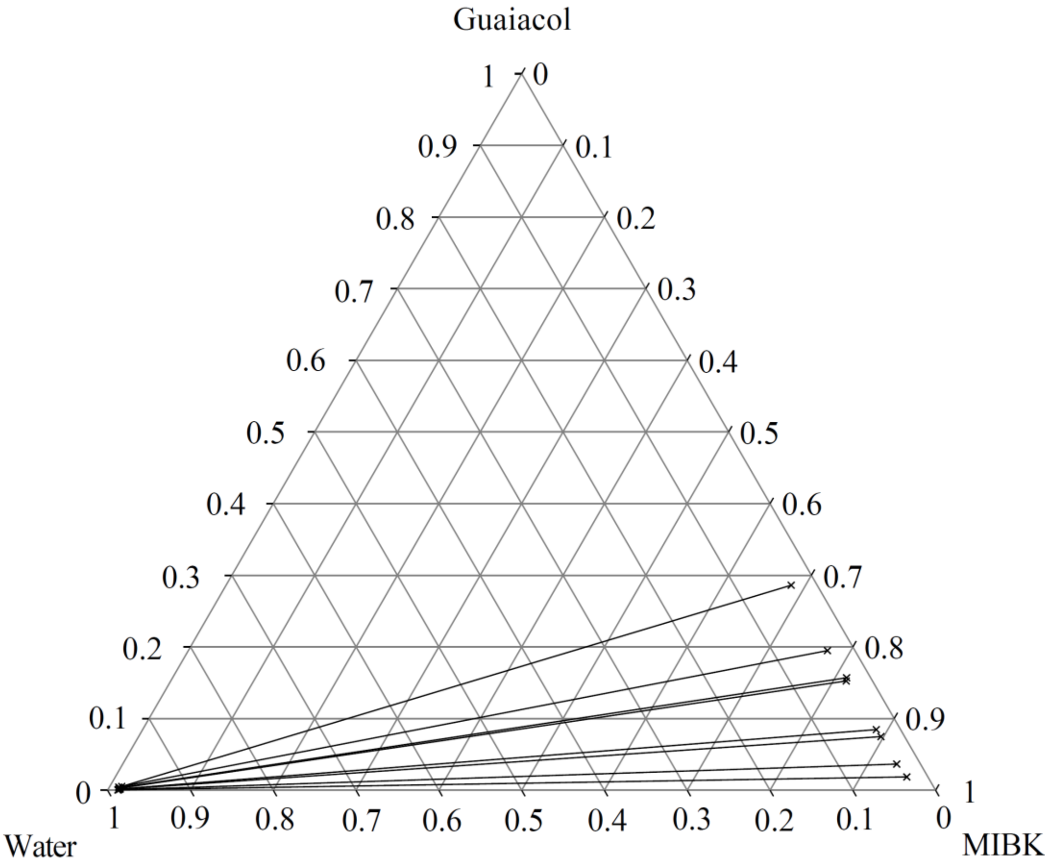

Figure 3.6: Ternary diagram of mass fractions for the system Water – Guaiacol – MIBK at 55 °C

3.1.3. Further Data Investigation

Some potentially interesting data analysis was inspired by the initial literature review that was performed for this project. This entailed the comparison of the compositional changes in the two liquid phases and well defined trends of increase or decrease for one component of the ternary system compared to another.

Initially in literature [22- 25] is reported that in the organic phase when the phenolic mass fraction is increasing the water also follows the same trend. Figure 3.7 and Figure 3.8 show the mass fraction of water ($w_{1,b}$) and guaiacol ($w_{2,b}$) plotted against the solvent to feed ratio (S/F) at 30 °C. In both cases the mass fraction of guaiacol is decreasing substantially since it is dilute in a higher amount of organic phase. That decrease is followed by a smaller decrease in the water mass fraction which suggests that the presence of guaiacol increases the solubility of water in this mixture. That can also be verified by the fact that according to literature [38] the solubility of water in MIBK expressed in mass fraction is approximately 0.016 and 0.024 for temperatures 30 and 55 °C respectively. The value that was measured by Karl Fischer for all the runs was always above the literature values for the binary system MIBK-water.

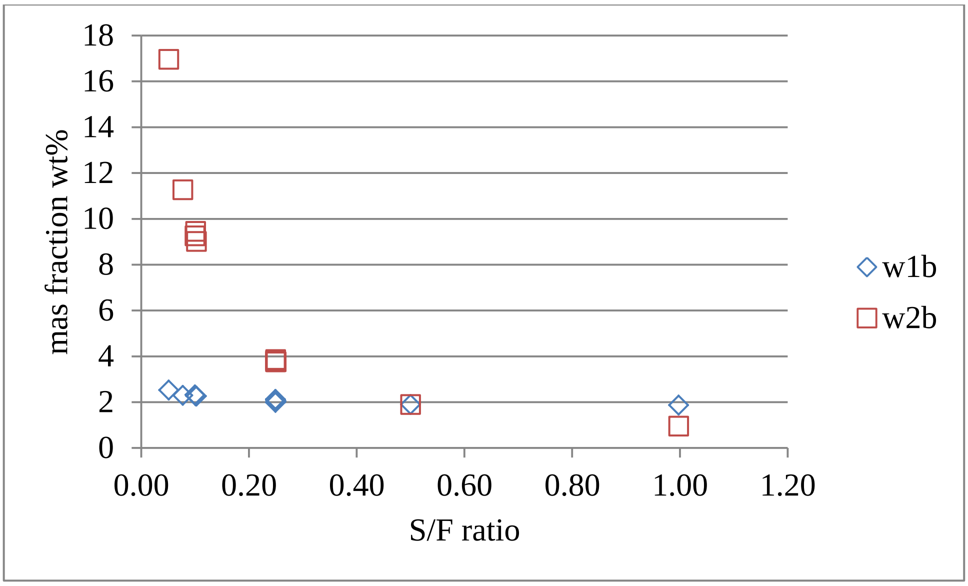

Figure 3.7: Mass fraction of water and guaiacol in the organic phase at 30 °C and for 1% w/w feed stock solution

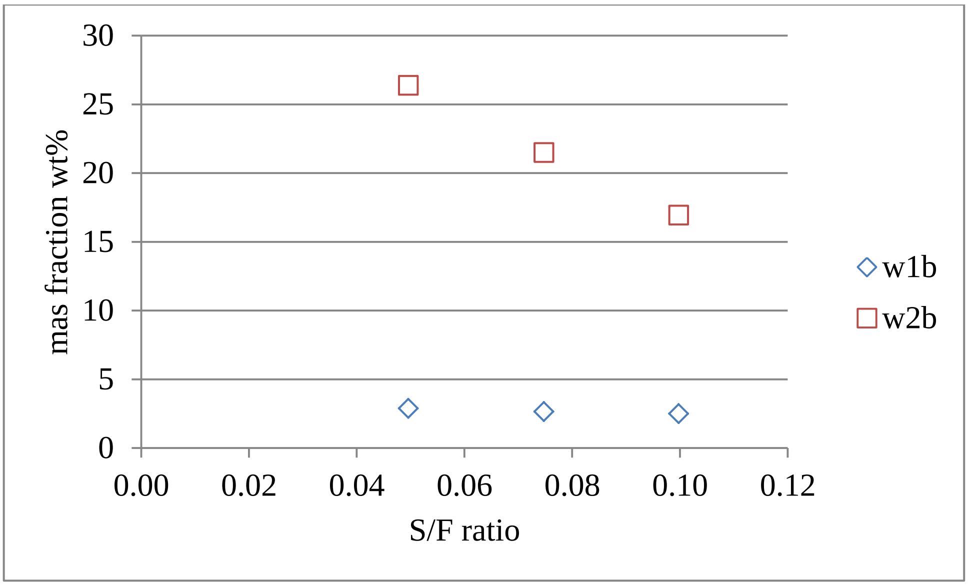

Figure 3.8: Mass fraction of water and guaiacol in the organic phase at 30 °C and for 2% w/w feed stock solution

In Figure 3.9 and Figure 3.10 similar plots are shown this time for the temperature 55 °C. The same trend exists also with the water mass fraction slightly decreasing as the guaiacol mass fraction decreases.

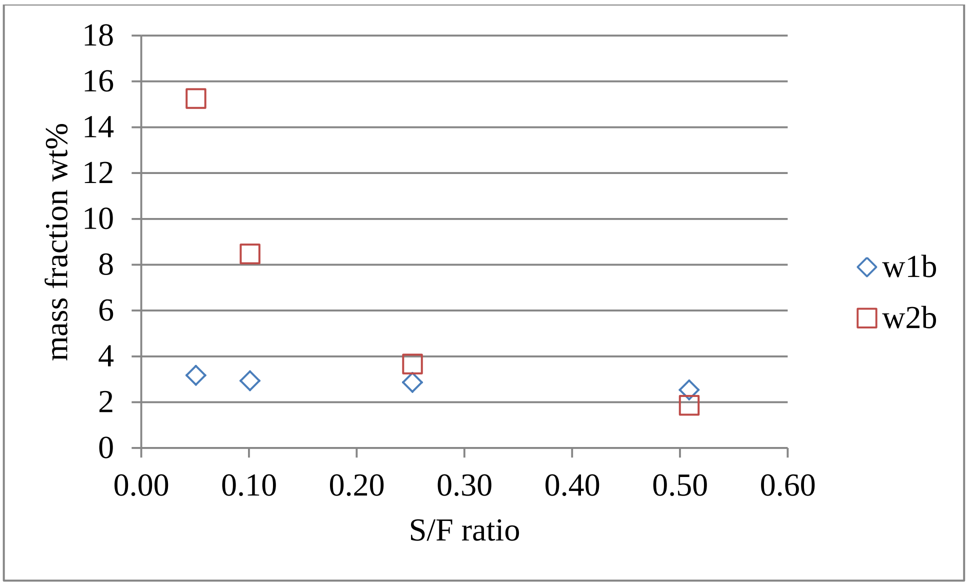

Figure 3.9: Mass fraction of water and guaiacol in the organic phase at 55 °C and for 1% w/w feed stock solution

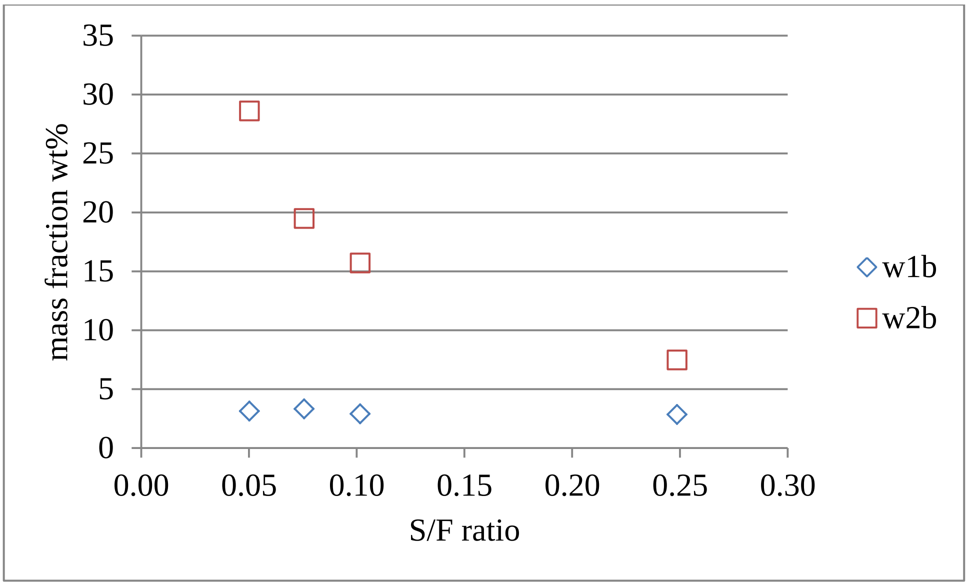

Figure 3.10: Mass fraction of water and guaiacol in the organic phase at 55 °C and for 2% w/w feed stock solution

Another observation of the literature [22- 25] was that in the aqueous phase the trend of the phenolics is typically the opposite of the solvent. When the mass fraction of a phenolic increased, then the solvent’s mass fraction decreased. As is shown in Figure 3.11 and Figure 3.12 this is also verified by this work for the experimental extractions at 30 °C.

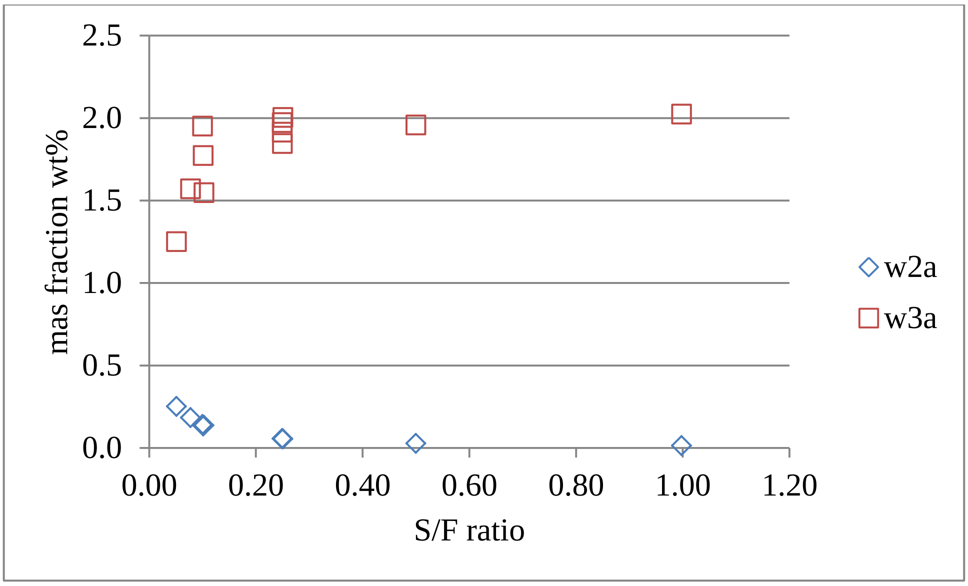

Figure 3.11: Mass fraction of guaiacol and MIBK in the aqueous phase at 30 °C and for 1% w/w feed stock solution

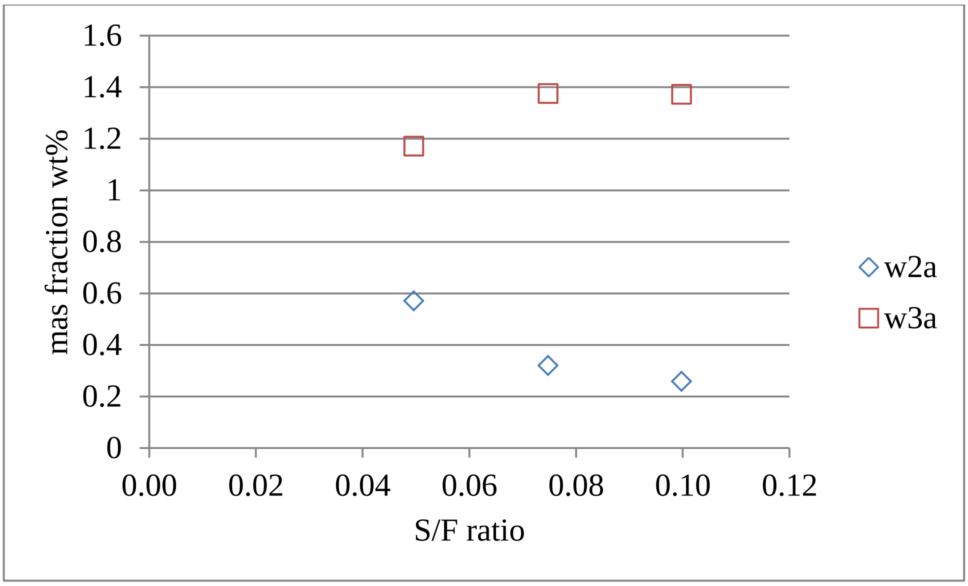

Figure 3.12: Mass fraction of guaiacol and MIBK in the aqueous phase at 30 °C and for 2% w/w feed stock solution

However in the case of the experimental runs at 55 °C the results were not so clear. The reason was that the gas chromatograph (GC) measurements were not always completely accurate, as it was mentioned in section 2.5.1. Because of this, one of the main advantages of the procedure adopted for this project was used. The phase fraction (α) that was calculated for each extraction experiment was used in order to calculate an ideal mass fraction for MIBK in the aqueous phase.

It was assumed that the mass of MIBK added in each extraction was accurately measured by the analytical balance. Additionally, the measured by the GC mass fraction of guaiacol in the organic phase and the measurement of water by the Karl Fischer titration were assumed accurate. Using the calculated mass fraction of guaiacol in the organic phase, the mass of guaiacol was calculated. Ultimately, the calculated MIBK mass in the organic phase was subtracted from the original MIBK mass and the mass fraction for the aqueous phase was calculated by:

$$w_{3,a}^{calc} = \frac{m_{3,a}^{calc}}{m_{aq}} \qquad [3.8]$$

Where:

- $w_{3,a}^{calc}$: Calculated mass fraction of MIBK in aqueous phase
- $m_{3,a}^{calc}$: Calculated mass of MIBK in aqueous phase (g)
- m_{aq} : Measured mass of aqueous phase (g)

The values for the mass fraction of MIBK that were calculated were plotted against the S/F in addition to the GC resulting mass fractions in Figure 3.13 and Figure 3.14.

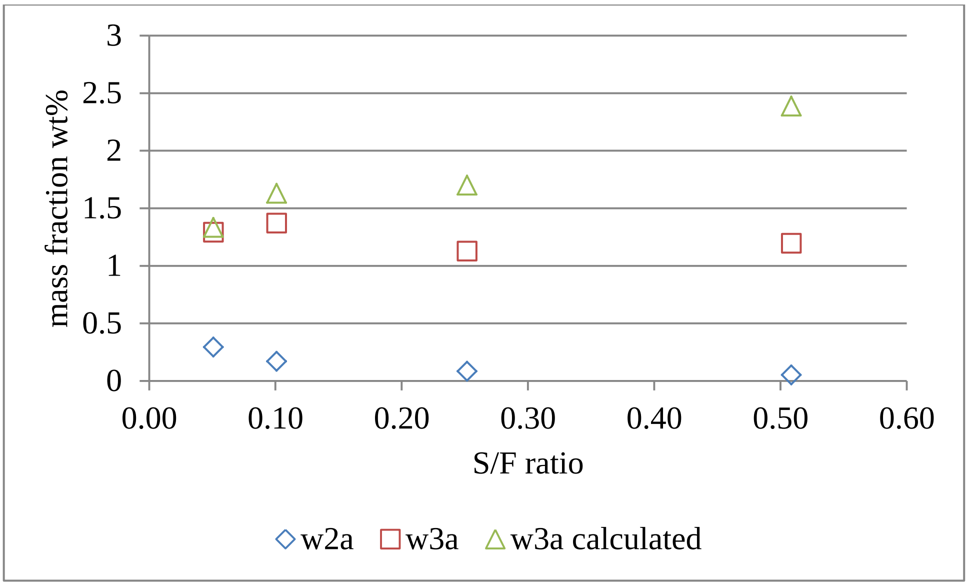

Figure 3.13: Mass fraction of guaiacol and MIBK (measured and calculated) in the aqueous phase at 55 °C and for 1% w/w feed stock solution

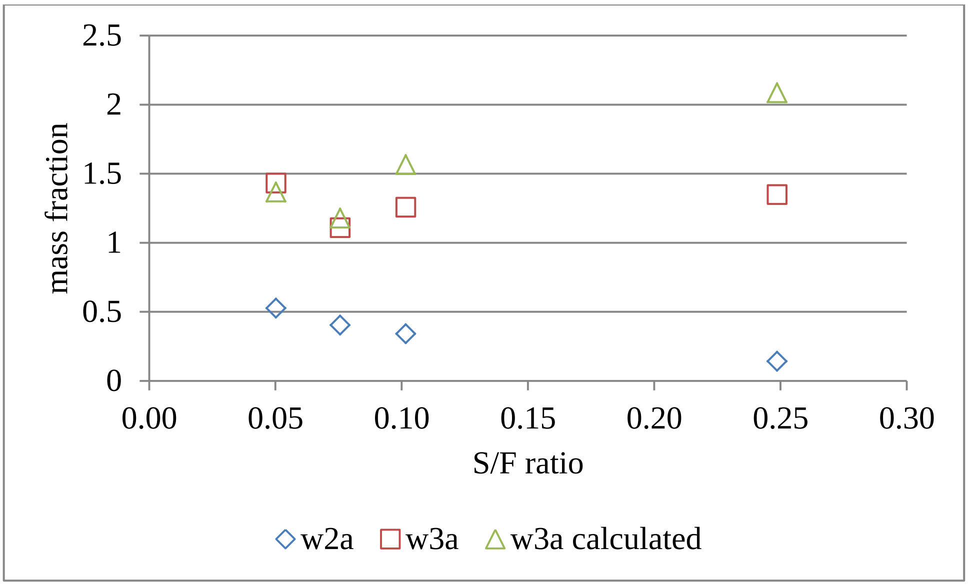

Figure 3.14: Mass fraction of guaiacol and MIBK (measured and calculated) in the aqueous phase at 55 °C and for 2% w/w feed stock solution

These two diagrams show that the calculated values of MIBK verify the expected trend in the majority of the experimental runs. In general, since the results at 30 °C are in agreement with literature for similar ternary systems it was assumed that this should be the trend of change between water and guaiacol. This assumption suggests that the issue could be mitigated by a number of changes in the method of GC analysis that may be used in further work, since time limitation did not allow the application of such changes. These changes are discussed in the perspective section of this report as suggestions for future work.

Chapter 4

4. Conclusion

The work of this project was based on the definition of the problem which was:

"Develop and utilize a laboratory scale liquid-liquid extraction method for Guaiacol by using Methyl Isobutyl Ketone (MIBK) as an organic solvent. The method should provide accurate experimental liquid-liquid equilibrium data for the ternary system Water-Guaiacol-MIBK."

This project was based on the study of an aqueous stream that is present in the process of the hydrothermal conversion of lignin to liquid fuel and industrial chemicals. The recovery of phenolic components is a part of optimizing the process in order to make it economically feasible. The recovery is typically performed by liquid-liquid extraction with the use of an organic solvent. The aspects that have to be studied in such a case are the performance of different solvents and the modeling of the system. Both of the above require accurate liquid-liquid equilibrium data for the system.

Since this is a complicated multicomponent system, the typical strategy is the study of individual ternary systems that can be combined using an appropriate thermodynamic model which can simulate the original system. In this case such systems contain water, an individual phenolic component and an organic solvent used for the extraction. After the necessary literature study it was indicated that for some of the phenolics there are no experimental data at all and one of the most prominent components was guaiacol. Additionally, the literature indicated that Methyl Isobutyl Ketone (MIBK) is a promising solvent for extraction purposes. Therefore the work of this project was focused on the acquisition of liquid-liquid equilibrium experimental data for the ternary system Water – Guaiacol – MIBK.

In order to succeed to the above, a procedure was planned for the liquid-liquid extraction and the acquisition of the equilibrium data. The procedure that was adopted was able to give good equilibrium results. The results were used to study the effectiveness of MIBK for the extraction of guaiacol from water. It was observed that MIBK is able to extract a high percentage of guaiacol (up to 96%) considering the single stage procedure and the operating conditions that were applied in this project.

Performing similar experiments in the two different temperatures it was observed that the extraction may be more successful in the lower temperature (30 °C). However, the absolute differences between the two temperatures were low to give definitive choice between the two. The lower temperature can also have the advantage of lower loss due to evaporation but for the experimental setup used in this project this was not an issue since sampling could be done in closed containers.

Regarding the industrial process of extraction, the initial temperature of the aqueous stream exiting the reactor can be as high as 600 °C. That could mean that the highest acceptable temperature for the extraction would be the prevalent choice since it would need less cooling for the extraction process and less heating power when it is recirculated to the hydrothermal process.

The comparison of present results with literature experimental data, for similar systems, showed a reduced extraction capacity of MIBK for guaiacol in comparison to other phenolic molecules like phenol or cresols. However, the extraction yield is sufficiently high and since guaiacol is one of the most valuable of the phenolic components, MIBK remains one of the most successful extraction solvents that are available.

In total the procedure that was used in this project was deemed satisfactory in many levels. The use of separation funnels as an equilibrium vessel gave the advantage of enabling an accurate measurement of the mass of the two liquid phases. This was an apparent advantage in the evaluation of the experimental runs by mass balances. In the case of the present work, since the weight measurement was assumed accurate, the phase fraction (α) could be used as a contingency measure when some of the gas chromatography results seemed dubious. In that aspect, it was used to calculate the mass fraction of MIBK in the aqueous phase for the experiments at 55 °C when they were observed to divert from an expected trend.

Another advantage of the procedure used in this project was the measurement of the water mass fraction in the organic phase by Karl Fischer Titration (KF). KF is considered very accurate and in this work it was evaluated as such. This fact, coupled with the consistency of the Gas Chromatography (GC) measurements for the organic phase made the final results for the organic phase very trustworthy.

Concluding, during the work that took place for this project, it was possible to acquire liquid-liquid equilibrium data for a ternary system that is relevant to the downstream process of hydrothermal conversion of lignin. This kind of data is valuable in the effort to make biomass a viable source of fuel and valuable chemicals. An additional value to this work is that the data acquired are not only valuable in the specific process but also in other industrial processes. For example the removal of phenolics from water is a standard process in the petroleum refining industry and petrochemical manufacturing since they are considered pollutants. In a lot of cases the concentrations are high enough that propose added value by recovering them instead of applying degradation methods.

Chapter 5

5. Perspective

During the experimental work of this master thesis project certain ideas were presented for the expansion or the optimization of procedures that were used.

Regarding further work:

The ultimate goal of the acquisition of liquid-liquid equilibrium experimental data for ternary systems is for them to be used in conjunction with thermodynamic models in order to simulate an industrial process. In this case the liquid-liquid extraction of numerous phenolic components that exist in an aqueous process stream. The thermodynamic correlation of data offers a powerful tool for process simulation which is essential in all industrial processes. For the ternary system that was chosen for this project, and optimally after the acquisition of a few more experimental data points, binary interaction parameters could be calculated and used with an appropriate thermodynamic model.

The literature study showed that some of the relevant phenolic components have not been studied in this frame. Phenol, guaiacol, catechol and cresols are the most abundant components found in the aqueous phase of the lignin conversion process. Since liquid-liquid equilibrium data for catechol are not available in literature, it would be very relevant to perform a similar study for the ternary system Water – Catechol – MIBK.

An interesting study related to the present work might be the liquid-liquid extraction of quaternary systems with more than one phenolic component. This could show how the presence of one phenolic changes the behavior of another. In addition, the aqueous phase of an actual lignin hydrothermal conversion system could serve as feed for extraction experiments. These two considerations could be used also as a validation for the potential modeling of the system.

Except temperature it is expected that the pH on which the extraction is taking place can be an affecting factor for the liquid-liquid equilibrium conditions. The experimental data in this work were performed in slightly acidic conditions since the water-guaiacol stock solution had an average pH of 5.5. Literature suggests that the actual process stream contains potassium carbonate which increases the pH and makes it alkaline [11]. Therefore a study of the pH effect to the extraction process would be interesting for future expansion of this work.

Regarding the modification of the procedure that was used for this project:

A few adjustments to the experimental setup could make a more convenient procedure. It was observed that the use of separation funnels provide certain advantages compared to setups used by other authors. A possible modification could be on the method of mixing by using a mechanical stirrer that could be attached to the funnel cap from above. In this way the stirring could take place for a long time in the set temperature and in a separation funnel.

Appendix I. GC Program and Standard Solutions

α. Gas Chromatograph Program

The gas chromatograph that was used throughout the analytical measurements of this project was programmed as follows. The initial temperature of the oven of the GC was kept for 1 minute at 110 °C. Then the temperature was increased at a rate of 30 °C per minute up to 250 °C and it was kept at this temperature for 1 minute. The injector temperature was 250 °C. The split ratio was kept constant throughout the measurements at the value of 50 and the pressure of the column at 10 psi.

β. Standard Solutions

Guaiacol in the organic phase

The standard solutions that were used for the calibration of the GC for the measurement of guaiacol concentration in the organic phase, were produced as follows.

A stock solution of $22.2\ \frac{g}{L}$ of guaiacol diluted in pure methyl isobutyl ketone (MIBK) was produced. Additionally a stock solution of the Internal Standard (IS) was produced with $15\ \frac{g}{L}$ of bromobenzene diluted in pure MIBK.

The standard solutions that were used are reported in the following table.

Table 5.1: Standard solutions for the analysis of Guaiacol in the organic phase

Standard	**Guaiacol Stock $\mathbf{22.2\ \frac{g}{L}}$** (ml)	**IS- Stock $\mathbf{15\ \frac{g}{L}}$** (ml)	**MIBK** (ml)	**Guaiacol** $\left(\frac{g}{L}\right)$	**Brombenzene (IS)** $\left(\frac{g}{L}\right)$
Std 1	0.50	5.00	4.50	1.11	7.50
Std 2	1.00	5.00	4.00	2.22	7.50
Std 3	3.00	5.00	2.00	6.66	7.50
Std 4	5.00	5.00	0.00	11.1	7.50

Guaiacol and MIBK in the aqueous phase

Similarly to the above mentioned procedure the standard solutions to calibrate the GC for the concentration measurement of guaiacol and MIBK in the aqueous phase were as follows.

A stock solution of 8.88 $\frac{g}{L}$ guaiacol and 8 $\frac{g}{L}$ MIBK diluted in distilled water were produced. Additionally a stock solution of the Internal Standard (IS) was produced with 8 $\frac{g}{L}$ of methyl ethyl ketone (MEK) diluted in distilled water. The standard solutions that were used are reported in the following tables.

Table 5.2: Standard solutions for the analysis of Guaiacol and MIBK in the aqueous phase

Standard	**Guaiacol & MIBK stock $\mathbf{8.88\ \frac{g}{L}\ \&\ 8\ \frac{g}{L}}$** (ml)	**IS – Stock $\mathbf{8\ \frac{g}{L}}$** (ml)	**Distilled Water** (ml)	**MIBK** $\left(\frac{g}{L}\right)$	**Guajacol** $\left(\frac{g}{L}\right)$	**MEK (IS)** $\left(\frac{g}{L}\right)$
Std 1	0.05	5.00	4.95	0.04	0.044	4.00
Std 2	0.10	5.00	4.90	0.08	0.088	4.00
Std 3	0.50	5.00	4.50	0.40	0.444	4.00
Std 4	1.00	5.00	4.00	0.80	0,888	4.00
Std 5	3.00	5.00	2.00	2.40	2.660	4.00
Std 6	5.00	5.00	0.00	4.00	4.440	4.00

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