

# Catalytic hydrotreating of lignin

By

Markus Lilja

Department of Chemical Engineering  
Lund University  
September 2019

Supervisor: **Associate Professor Christian Hulteberg**

Co-supervisor: **Linnéa Kollberg**

Examiner: **Postdoc Sara Blomberg**

**Postal address**

P.O. Box 124  
SE-221 00 Lund, Sweden

**Web address**

[www.chemeng.lth.se](http://www.chemeng.lth.se)

**Visiting address**

Naturvetarvägen 14

**Telephone**

+46 46-220 82 85

+46 46-220 00 00

**Telefax**

+46 46-220 45 26

## Abstract

One of the main challenge's society faces today is climate change caused by CO<sub>2</sub> due to the dependence on fossil fuels. To combat the increasing CO<sub>2</sub> levels there is a need to develop renewable fuels. One such fuel could potentially be derived from lignin.

In this thesis, lignin derived from a pulp and paper mill was first treated and cleaned. The lignin was then processed by catalytic hydroprocessing. By varying time as well as the amount of H<sub>2</sub> within the decided central composite design, the future direction of further could be discovered. For each experiment there was a comparison test conducted (blank) without lignin conducted in order to examine the effect of the lignin. The resulting products were analysed by GC-Fid through comparison to biodiesel as well as commercial gasoline. Afterwards mass balances were used to analyse the yields.

The results of the experiments indicated that the set interval of parameters or equipment were not optimal for lignin. Since they resulted in a large amount of coke formation, especially in the cases of more severe treatment. For future research the results seem to point towards the use of higher content of H<sub>2</sub> coupled with shorter reaction time.

However, different catalysts, equipment setups as well as lower temperatures will need to be evaluated for lignin fuel optimization.

## Acknowledgments

This master thesis was carried out at the Department of Chemical Engineering at Lund University in close collaboration with SunCarbon AB as well as Hulteberg Chemistry & Engineering AB. I am grateful for having had the opportunity of working in such an exciting field as producing fuel from lignin as my master thesis.

Special thanks to Linnéa Kollberg at SunCarbon for all your help, guidance and support during this thesis.

I would like to thank Christian Hulteberg for the many theoretical discussions regarding possibilities, analysis as well as general guidance.

I would also like to thank Martin, Daniela and the team at SunCarbon in Piteå for their help with the ICP-OES analysis.

Furthermore, I would like to thank Andreas Leveau for all the practical help associated with the experiments and analysis. Lastly, I would like to thank Emil, Jon, Jakob and Fiznik at Hulteberg in Tygelsjö who brightened up every workday as well as withstanding my dry sense of humour.

# Popular science summary: Catalytic hydro-processing of lignin

**By using lignin, which is a byproduct of the pulp and paper industry, there is hope of reducing the world's dependency on fossil fuels. In this work, lignin was broken down by hydrogen and heat to produce fuel. The results suggest higher amounts of hydrogen at lower temperatures as the direction of further work.**

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One of the largest challenges that is discussed today, is that of climate change. According to the United Nations [1], “*Climate Change is the defining issue of our time and we are at a defining moment. From shifting weather patterns that threaten food production, to rising sea levels that increase the risk of catastrophic flooding, the impacts of climate change are global in scope and unprecedented in scale. Without drastic action today, adapting to these impacts in the future will be more difficult and costly*”. Climate change is mainly caused by the burning of fossil fuels, which today covers a lot of the world's energy demand. By burning fossil fuel, CO<sub>2</sub> is released into the atmosphere, which has been stored in the earth's crust for millions of years. The increased CO<sub>2</sub> in the atmosphere then traps more of the sun's energy, which leads to increased temperatures around the globe. To prevent further increase in temperature, while continuing to enable our way of life, there is a need to find renewable sources of fuels.

Such renewable fuels could be made from wood, which takes us to the remarkable molecule of lignin. Lignin makes up roughly a third of all the contents of wood. Interestingly, other than being a renewable source, it is already being produced in huge quantities around the world, since in the making of paper, it needs to be removed. This means that lignin is available in huge quantities, which if converted to fuel, would enable large quantities of fossil fuels being left in the ground. Before lignin can be used for fuel, it needs to be broken down into smaller molecules of the right size. For this sake, lignin was treated by H<sub>2</sub> at high temperatures and the products were evaluated.

The results showed that the selected duration of experiments and/or possibly the temperature was set to high. This was shown by the unwanted gas and coke content, which increased the longer the experiments took. Furthermore, it was also shown that higher H<sub>2</sub> pressure led to less gas and coke being formed from lignin. Nonetheless, the results showed fuel being made from lignin, which was seen in the experiments with the lowest duration and at the highest H<sub>2</sub> pressure. This means that future experiments should be done in those directions. However, during experimentation and evaluation, several issues arose with the method and equipment, which could affect the results. For example, the heater couldn't sometimes keep the temperature up, there were large variations in results of repeated experiments, many leaks were detected, and it took a long time heat up and cooldown the reactor. This means that a different experimental setup might be desirable in future experiments.

The conclusion that can be drawn is that lignin is an exciting field with lots of potential, and we might be one step closer to a world that is free of fossil fuels. However, there is much more work that needs to be done in the field of making fuel from lignin.

# Abbreviations

BL	Black liquor
C	Carbon
CO <sub>2</sub>	Carbon dioxide
FAO	Food and Agriculture Organization of the United Nations
GHG	Greenhouse gases
H <sub>2</sub>	Hydrogen gas
HT	Hydrotreating
HGL	Hydrogenolysis
HG	Hydrogenation
HDS	Hydrodesulfurization
HDO	Hydrodeoxygenation
HDN	Hydrodenitrogenation
mb/d	Million barrels per day
mt/y	Million tons per year
N	Nitrogen
NaOH	Sodium hydroxide
Na <sub>2</sub> S	Sodium sulphide
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate
MeOH	Methanol
O	Oxygen
OPEC	Organization of the Petroleum Exporting Countries
POLO	SunCarbon process: Purification of Lignin oil
S	Sulfur
SOLO	SunCarbon process: Separation of lignin oil process
UN	United Nations
VGO	Vacuum gas oil
W%	Weight %

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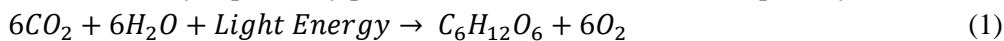
# 1 Introduction

The world of today and tomorrow faces challenges that must be addressed in order to secure the future of mankind. The challenges are, but not limited to, climate change, the dependence on fossil fuel, agricultural and food security.

As written on the website of the United nations (UN), “*Climate Change is the defining issue of our time and we are at a defining moment. From shifting weather patterns that threaten food production, to rising sea levels that increase the risk of catastrophic flooding, the impacts of climate change are global in scope and unprecedented in scale. Without drastic action today, adapting to these impacts in the future will be more difficult and costly*” [1].

Current climate change is due to the accumulation of greenhouse gases (GHG) in the atmosphere, especially carbon dioxide (CO<sub>2</sub>) which retains parts of the sun’s energy in the atmosphere. The man made main causes of increased GHG are the industrialization from the mid 1800’s, deforestation, agriculture, increased population and increasing living standards [1].

CO<sub>2</sub> is normally captured by plant cells. Which uses CO<sub>2</sub> in the photosynthesis, as seen in reaction 1.



Part of those plant cells then sediment on the ocean floor as layers of organic material. Over time more layers of varying materials are added, which leads to increasing temperatures and pressures. Over long stretches of time, the organic material is then turned into fossil fuels such as oil. Thus, the CO<sub>2</sub> in the atmosphere is deposited in the earth’s crust.

With the increase in world population as well as rising living standards, the combustion of fuels such as oil, petroleum and coal has risen. The CO<sub>2</sub> is thereby released into the air again, as illustrated by reaction 2 showing complete combustion.



*x and z are numbers associated for a given molecule in a fuel. y is the stoichiometric ratio for the complete combustion of that molecule.*

According to the Organization of the Petroleum Exporting Countries (OPEC) [2], the energy demand by 2040 will increase by 35 % compared to 2015, of which oil constitutes roughly 27.1 %. Furthermore, the overall oil demand is projected to increase from 95.4 million barrels per day (mb/d) in 2016 to 111.1 mb/d (increase of 16.6%) by the year 2040. Thus, the released CO<sub>2</sub> from fossil fuel can be expected to increase in the future.

One way to combat the increasing CO<sub>2</sub> levels in the atmosphere is to find fuels which are not made from fossil fuel. One such fuel could potentially be economically viable derived from lignin, which has interesting chemical possibilities, which is discussed in section 2.1.3.

Lignin is a biproduct in the form of black liquor in the pulp and paper industry, which is burnt in the Kraft process (section 2.2).

Processing of black liquor from the Kraft process was about 170 million tons per year (mt/y) in 2001 with a predicted production over 250 mt/y by 2025. Which indicates that pulp and paper by Kraft processing is a growing business [3].



Also, according to the Food and Agriculture Organization of the United Nations (FAO), the global paper and paperboard production is predicted to increase in the future. Which means that lignin from the pulp and paper industry is and will be available in the future [4].

An ethical issue with biofuels in general is that they many times compete with food security. This means that so-called first-generation biofuels, which are for example produced from starch and sugars compete with food. There is for example bioethanol, which is produced from corn. This means that if the production of such a biofuel goes up, then the usage of corn increases as well. This in turn leads to shortage of food, but it also leads to increases in prices, both local and international. Said prices and shortages especially affect the poorest countries and the poorest groups of people. By utilizing second-generation biofuels from example lignin, such ethical dilemmas are mitigated [5].

## 1.1 Aim and limitations

The aim of this master thesis was to examine the effect of different process parameters on gasoline and diesel yield via catalytic hydrotreatment (HT) of lignin.

First lignin was pre-treated and mixed with vacuum gas oil (VGO), to simulate a usable lignin feed. The lignin feed as well as references of pure VGO were then hydrotreated at different durations, temperatures and H<sub>2</sub> pressures for evaluation. The evaluation was based on the yields of diesel and gasoline, as well as the yields of unwanted coke and gas.

Only initial evaluation of catalytic hydrotreatment was conducted in this thesis. Thus, no work on the method of lignin feed, scale-up, effect of different catalysts, catalyst life or optimization of specific high value molecules were conducted.

## 2 Background

In this section the background of lignocellulosic biomass, the Kraft process, pulp and paper environmental impact, the company SunCarbon, hydrotreating and catalyst will be briefly introduced. The theory regarding base catalysis, SOLO and POLO will not be elaborated in this thesis. However, the theory is available in a master thesis by Martin Sundin [6].

### 2.1 Lignocellulosic biomass

For thousands of years, human civilization has utilized lignocellulosic biomass in the form of wood and other fibrous materials. It has for example been used as building material, as fuel and for clothing. Human civilization and culture can therefore be said to have been shaped to a considerable extent by lignocellulosic materials [7].

Furthermore, lignocellulosic biomass is an abundant resource which makes up about 80 % of the world's biomass and is thus quite easily accessible in larger quantities [8].

Lignocellulosic biomass is a complex rigid structure, which is resistant to physical, biological and chemical degradation. It consists mainly of three types of polymers, which are cellulose, hemicellulose and lignin. The chemical features of lignocellulosic biomass are mainly dependent on the structure and compositions of the polymers. While the physical features are dependent on surface area, crystallinity, degree of polymerization, particle size, pore volume, and the distribution of lignin, hemicellulose and cellulose [9].

#### 2.1.1 Cellulose

Cellulose was first described in 1838 by the French chemist Anselme Payen, after extraction following treatment of wood with ammonia and acids. Structurally, cellulose is a linear polymer that consists of  $\beta$ -D-glucopyranose subunits which are linked by (1-4)-bonds. The chemical structure of cellulose can be seen in Figure 1. Cellulose exists in nature in several forms which are either amorphous or crystalline to varying degrees. The degree to which cellulose crystallize depends on how the many hydroxyl groups interact, the degree of polymerization, but also on how each of the subunits of cellulose are related to each other in the overall structure. The role cellulose has in wood is to provide structural strength. Given this strength, cellulose is the most important ingredient in for example paper, giving paper its structural strength [9].

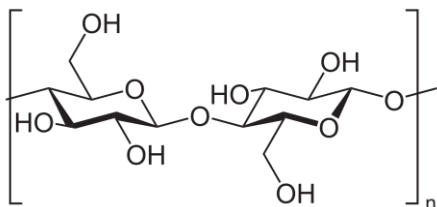


Figure 1. Chemical structure of cellulose [10].

#### 2.1.2 Hemicellulose

Hemicellulose is a term for heteropolysaccharides consisting of a wide variety of monosaccharides such as  $\alpha$ -D-glucopyranose,  $\beta$ -D-mannopyranose and  $\alpha$ -D-xylopyranose to mention a few. Structurally hem-

icellulose is branched molecular network in contrast to the unbranched network of cellulose. One example of the structure of hemicellulose can be seen in Figure 2. Wood usually consists of about 20-30% of hemicellulose [11].

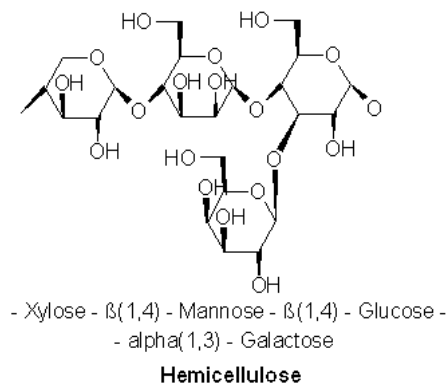


Figure 2. Example of chemical structure of hemicellulose [12].

Most importantly what hemicellulose does, is that it provides strength to the cell wall, by enabling the interaction of cellulose and lignin in certain cell walls [13].

### 2.1.3 Lignin

Generally, lignin is described as a polyphenolic biopolymer made of the three monomers of coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol, seen in Figure 3 [14].

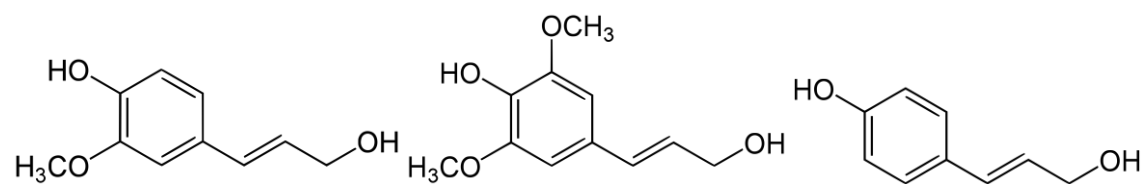


Figure 3. Chemical structure from the left to right of coniferyl alcohol sinapyl alcohol and p-coumaryl alcohol. Modified from [15]–[17].

How lignin is synthesized in plant cells is under debate; however, it is commonly thought to be the results of random radical coupling reactions, water addition and reactions of the hydroxyl groups located at various sites on the monomers. Said reactions results in network with no repeating units. In addition, the occurrence of the monomers in lignin differs a lot depending from where the lignin is derived. Hardwood lignin's contain mostly coniferyl alcohol and sinapyl alcohol while normal softwoods contain >90 % coniferyl alcohol [14].

Looking at the structural example of lignin (Figure 4), if all oxygen in the ether bonds (Figure 5) are removed from the structure what comes out are molecules consisting of 12 carbon atoms or less. Which is interesting since gasoline consist mostly of 4-12 carbon atoms.

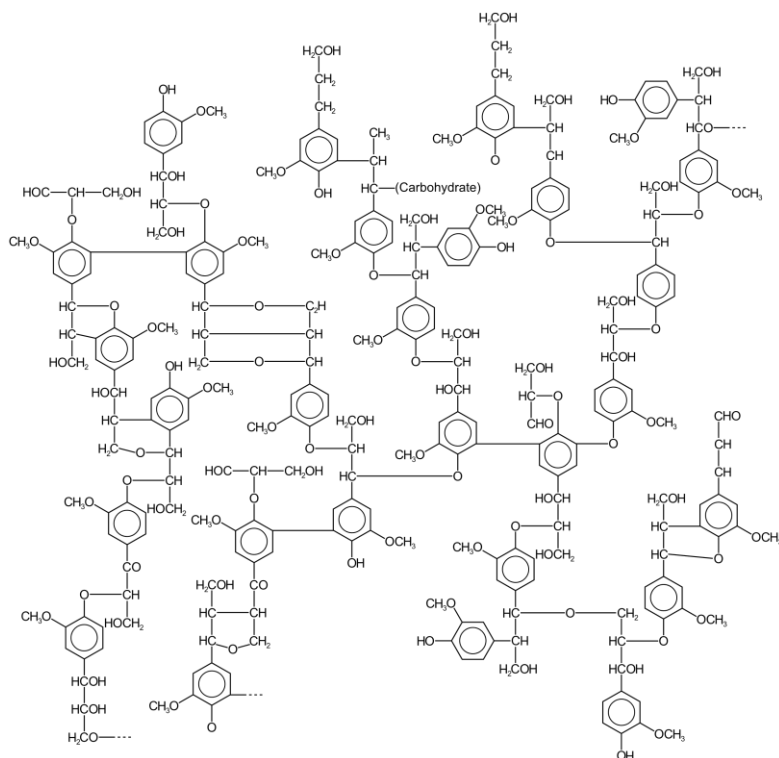


Figure 4. Chemical structure of lignin [18].

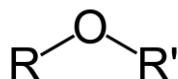


Figure 5. Structure of ester bonds with  $R$  and  $R'$  being either alkyl or aryl groups [19].

Each individual bond in lignin has different thermal properties [20]. Therefore, they require varying degrees of energy in order to break. However, it is not necessarily a problem if only parts of the ether bonds are broken, because another interesting carbon range is that of C12-C20, which is the range of diesel fuels. This means that lignin has the potential to act as a substitution for fossil fuels, and that optimization fitted to the fuel demand is possible.

One of the functions that lignin has in lignocellulosic biomass is that it provides structural support. As an example, perennial plants like trees has a higher amount of lignin in contrast to for example grass. Softwood consists of roughly 24-33 dry w % lignin, while hardwood consists of 19-28 dry w % of lignin. A downside with the abundance of lignin is that it usually surrounds both cellulose and hemicellulose. Therefore, processes which require low amounts of lignin, such as the pulp and paper industry, need to use processes such as the Kraft process in order to remove the lignin [8], [14].

## 2.2 Kraft process

The Kraft process is a process in which wood is made into pulp. Specifically, it is the process in which lignin and hemicellulose is removed from cellulose, since too much lignin and hemicellulose results in poor paper quality. First woodchips are treated by cooking chemicals, commonly referred to as white liquor, which is an aqueous solution of sodium hydroxide (NaOH) and sodium sulphide (Na<sub>2</sub>S). The woodchips and white liquor are then treated in a pressurized vessel known as a digester, at temperatures of about 170 °C. The most important of what happens in the digester step is that lignin is fragmented by

hydroxyl (OH<sup>-</sup>) and hydrosulphide (SH<sup>-</sup>) ions, followed by solvation of the lignin into the alkaline solution [21].

Next is the washing step, where the wood pulp is separated from the alkali solution, which is now called black liquor (BL). Since BL contains the cooking chemicals, they need to be recovered and reused for a feasible process.

First, the water content is reduced by utilization of several evaporators operating at various pressures and temperatures. The resulting heavy BL of about 65 % solid particles is then sent to the recovery boiler. The purpose of the recovery boiler is to recover the cooking chemical, but also to generate steam and electricity for the pulp and paper plants. In the recovery boiler, the heavy BL is sprayed and burned in an oxygen poor area, resulting in the formation of Na<sub>2</sub>S. The smelt in the bottom of the recovery boiler, containing mostly of Na<sub>2</sub>S and Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) is then mixed with water, at which point it is commonly referred to as green liquor. The green liquor is then treated in the causticizing plant with lime, in which NaOH is recovered from Na<sub>2</sub>CO<sub>3</sub> to which the original white liquor is recovered. Furthermore, the lime is also recovered in a lime kiln at high temperatures. A simplified schematic of the Kraft processes and its steps is seen in Figure 6 [22].

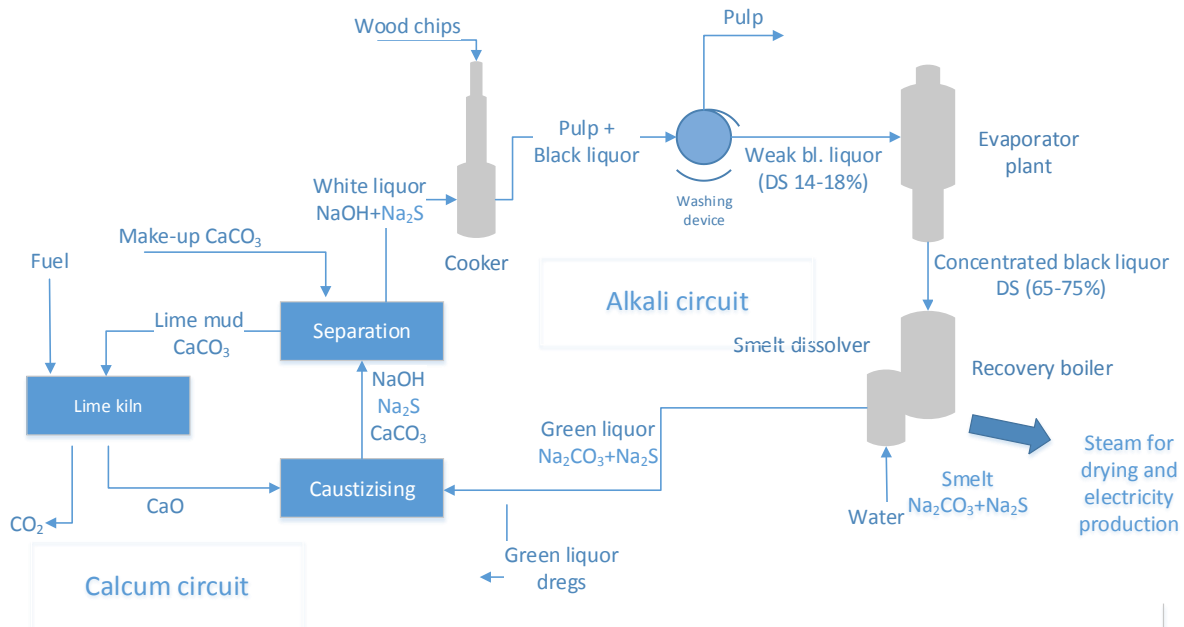


Figure 6. Simplified schematic illustrating the different stages in the Kraft process [23].

## 2.3 Pulp and paper environmental impact

This section was added with the purpose of shedding some light to the global situation regarding the pulp and paper environmental impact.

The pulp and paper industry are a well-known source of pollutants such as hydrogen sulfide (H<sub>2</sub>S), methyl mercaptan, chlorinated and organic compounds, sulfur and nitrogen oxides (SO<sub>x</sub>, NO<sub>x</sub>) and carbon dioxide (CO<sub>2</sub>). Studies have also shown various negative effects on marine life, regarding reproduction, for animals living downstream of pulp and papermills in the USA and Canada [24], [25].

According to U.S. Environmental protection agency, the pulp and paper industry in the U.S. is ranked number one in toxic weighted pound equivalents discharged into water. The discharge makes up 92 %

of the overall H<sub>2</sub>S and dioxin like substances. However, a noteworthy point is that out of 226 facilities, 7 facilities stands for 80 % of the H<sub>2</sub>S emissions and 5 facilities stands for 93 % of the dioxin emissions.

The pulp and paper industry also contribute to deforestation in countries such as Brazil, where farmers illegally clear forests to make way for crops and cattle. Forestry industries and the western civilization buys part of the cleared lumber and thus contributes in part to the deforestation in those areas [26], [27].

On the other hand Lhôte [28] claims that in Europe the forests increase in area. Furthermore, since 2005 the forests have grown by an area the size of Switzerland, all while the amount of lumber produced is increased as well as the area of forests being not worked by forestry industries. This due to political policies, good forest management, investments from sustainable forestry industries and landowners whom are acting with the goal of continued revenues.

In the USA, one of the major causes for deforestation and the spoiling of water sources is the clearing of forest for development of industries and housing. One way to preserve nature and water sources is to make it more attractive through incentives, especially for private land holders, to maintain their forests through sustainable forest management. Consequently the paper industry can assist in sustainability, if done right [29].

Regarding the environmental impact of forestry and the pulp and paper industry, what is interesting is that in the case of water pollution in the USA, only a few pulp and paper mills are responsible for most of the pollution. From this, improvements could be made to reduce those negative effects, should those mills be upgraded, exchanged or phased out to more modern ones with proper recycling and waste treatment, as in the case of Kraft cooking with recycled cooking chemicals as will be mentioned in section 3.2.

Furthermore, by creating incentive for land holders to switch to sustainable forest management, the pulp and paper industries can potentially help the environment, as it is done in many parts of Europe.

Another interesting aspect from an environmental point of view is that by making further use of biproduct streams such as lignin, there is the prospect of reducing the current fossil fuel demand in the transportation sector of the economy.

Thus, both the pulp and paper mills and the petroleum industry might become more environmentally friendly. While this thesis does not focus on other biofuels such as ethanol which can be derived from cellulose, it is worth mentioning that there is the possibility of further making the forestry industries such as pulp and paper or others even more sustainable by helping to reduce the dependence of fossil fuels through uses of other biproduct streams.

## 2.4 SunCarbon

SunCarbon AB is a company located in Lund Sweden, which was founded in 2014 by KIRAM, Hultberg Chemistry & Engineering AB and Arkel Innovations AB and currently owned by the founders as well as Preem AB and Sveaskog förvaltning AB. The company aim is to use the lignin by-product of the pulp and paper mills, which is currently being burned in order to recover the cooking chemicals in the Kraft process.

However, lignin is a compound with a lot of potential as previously explained, which could be used to produce a wide variety of chemicals and fuels. Thus, what SunCarbon AB aims to do is to purify and

make the lignin into a bio-oil, which is then sent to petrochemical refineries, where the bio-oil is subsequently made into fuel. The refineries have however set several requirements on the lignin bio-oil. Firstly, the lignin must be pumpable, preventing issues associated with powders, which currently other companies can provide. Secondly, the lignin must be purified of substances such as metals and sodium ions which pollute the catalysts used by the refineries. Furthermore, the pulp and papermills also have requirements. For instance, the cooking chemicals must be returned to their processes.

To overcome these and other challenges SunCarbon has developed a process, which first filters a part of the black liquor in a Kraft process by membrane filtration. The permeate which contains 80 % of the cooking chemicals and some lignin is sent back to the evaporators of the pulp and papermills. The lignin-enriched retentate on the other hand is further treated at an elevated temperature, where a base catalysis is conducted in order to depolymerize the lignin into smaller components. Following depolymerization, the resulting stream is then treated at a lower temperature with carbon dioxide, which is referred to as the separation of lignin oil process (SOLO). The solvation of the carbon dioxide into the stream subsequently leads to the formation of two phases, a lighter water phase, and a heavier lignin rich phase. The lighter phase is sent back to pulp and paper mill, while the heavier lignin phase is washed in several steps in what is called the purification of lignin oil process (POLO). After the washing, a carrier oil from the refineries is added for the purpose of solving the lignin into the final bio-oil.

## 2.5 Hydroprocessing

In this section the theory of the hydroprocessing methods of hydrogenation, hydrogenolysis, hydrodeoxygenation, hydrotreating and hydrocracking are briefly explained.

### 2.5.1 Hydrogenation

Hydrogenation (HG) is a reaction in which double-, triple bonds or aromatic structures are saturated by the addition of hydrogen. Often a catalyst is used to improve yields and selectivity.

Hydrogenation is a common process used by the petroleum industry as a way of upgrading fuels. The food industry uses hydrogenation as a means of saturating polyunsaturated fatty acids with the assistance of a nickel catalyst. By saturating the vegetable oils, their physical properties change in such a way that the fats are hardened and thus easier to use in applications such as bakery [30].

### 2.5.2 Hydrogenolysis

Hydrogenolysis (HGL) is a reaction in which C-C or C-heteroatom bonds are cleaved by hydrogen often by use of a catalyst. Most commonly it refers to the removal of sulfur (S), oxygen (O) or nitrogen (N), which are hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodenitrogenation (HDN) respectively. HGL is used by the petrochemical industry as a means of removing S and N-compounds that would otherwise poison catalysts as well as causing too high content of S in the product streams. Furthermore, HGL is also used to prevent build-up of coke onto the catalyst used in various processes such as steam reforming, thus prolonging catalyst life [31]–[33].

When it comes to bio-oils derived from lignocellulosic biomass, usually they have a low amount of S- and N-containing compounds. However, they suffer from various problems such as low energy density, viscosity and instability, due to high oxygen (O) content [31].

### 2.5.3 Hydrodeoxygenation

HDO is as mentioned the process in which C-O bonds are cleaved by hydrogen. Usually temperatures at 400-773 K are used at up to 200 bars hydrogen (H<sub>2</sub>) pressure [31].

According to a review by Furimsky [32], a key issue with HDO is understanding what kind of reactions that occurs. However, due to the complexity in analysing reaction mechanisms for complicated mixtures and structures, model compounds have often been used. Furimsky discussed the complexity of the relatively simple molecules of methyl phenols. According to him, one study found that by use of Ni-Cr catalyst, that o-methyl and p-methylphenol are more stable to HDO than phenol and m-methylphenol due to possibly steric hinderance. This result was corroborated by another study [34] which utilized Ni/SiO<sub>2</sub> catalyst.

Moreover, the complexity is further enhanced by what type of catalyst is used for the HDO. Zhan et al. [31] showed this in their review, in which guaiacol was tested in two experiments. This was done by varying only the catalyst used, under identical conditions, first by MoS<sub>2</sub> and then by CoMoS. MoS<sub>2</sub> yielded the major products of phenol, cyclohexane, benzene and methylcyclopentane, while CoMoS yielded only phenol and benzene. Thus, HDO of large structure such as lignin and all its possible products are complicated.

### 2.5.4 Hydrocracking/Hydrotreating

Hydrotreating and hydrocracking are two similar processes. Hydrocracking is a process in which heavy distillates and oils are cleaved into smaller molecules such as those present in gasoline and diesel. Hydrotreating on the other hand are processes in which impurities are removed (HDS, HDO, HDN). The main difference between hydrocracking and hydrotreating is the severity of the process. Meaning how long the reactants are kept at reaction temperatures, with hydrocracking being the more severe. Initially, olefins if present will be saturated (HG). Then as the severity of processing increases HDS, HDO and HDN occurs. Subsequently with further severity, hydrocracking is initiated, and the carbon bonds start to break down at a rapid rate. In the hydrocracking industry, the general design is that, first the feeds and catalysts are all preheated. They are then subjected to each other while heat is either increased or reduced, depending on the specification of the product. Furthermore, depending on the product specification, the process can be adjusted to meet the prerequisites [35].

## 2.6 Coke

Coke is a description for polyaromatic compounds, which are produced in a wide variety of processes in many industries, such as the petroleum industry. Coke causes process issues such as lower heat transfer, lowered yields, lowered selectivity, shorter catalyst life and process stops. To combat the formation and deposit of coke, various techniques are applied in industry such as coatings and selectivity control. Additionally, to counteract deactivation of catalysts what the petroleum industry gradually increases is the reaction temperature over time. However, this can result in an increase of coke formation, thus aforementioned problems are also increased over time. Most often coke is an undesired low value by-product mainly burnt as fuel for processes if at all possible. However in certain cases such as for electrode coke, it is of higher value due to its specific properties and composition [36].



## 2.7 Catalyst

A downside too many chemical reactions is that they often take too long time or have poor selectivity to a certain product. Thus, certain processes become unprofitable due to selectivity or time. To overcome these limitations catalysts are used. What catalysts does is that they lower the activation energy for certain reactions, thus making them happen faster, see Figure 7.

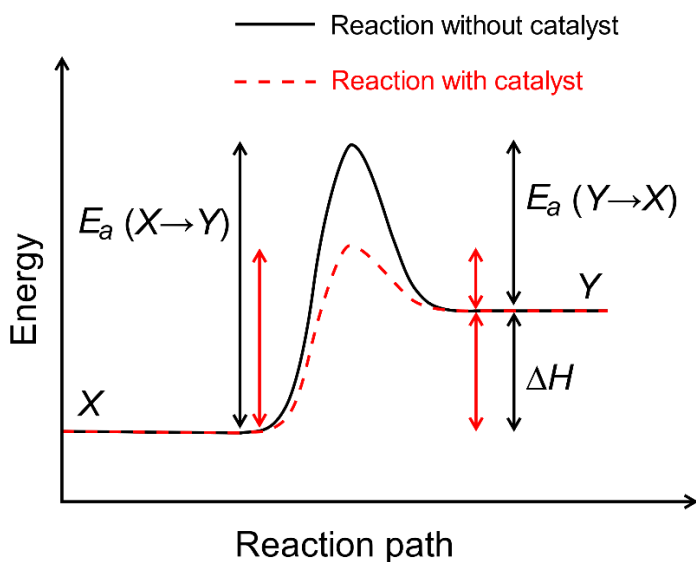


Figure 7. Shows how the activation energy  $E_a$  from X to Y or Y to X changes by adding a catalyst. X and Y can be either a reactant or a product. The enthalpy  $\Delta H$  is unchanged. [37]

A catalyst however does not change the equilibrium of the reactants and products. Meaning that if a process can react long enough, it will end up with the same result with or without a catalyst. However, this means that by stopping a reaction at a specific time, then the products can be tuned due to the different rates of reactions occurring [38].

## 3 Method

In this section, the methods used for the experiments are presented. First is the pre-treatment of the lignin. The pre-treatment starts with the preparation of the lignin by base catalysis followed by SOLO, which ends with a lignin powder. The pre-treatment section is ended by POLO, where the lignin is washed several times with sulfuric acid, methanol and deionized water, in order to remove unwanted substances. Following the pre-treatment section comes the focus of this study, which is the catalytic hydrotreatment of the washed lignin.

### 3.1 Pre-treatment

This section contains the pre-treatment methods of base catalysis, SOLO and POLO.

#### 3.1.1 Base catalysis and SOLO

First, a lignin rich retentate was retrieved from the Kraft process at the pulp and papermill located in Piteå in the north of Sweden. The retentate is then sent to SunCarbon's facility in Tygelsjö in the south of Sweden.

About 300 ml of the retentate was treated with base catalysis by chemicals already present in the retentate. This is done in a Parr 4570 series reactor at 230 °C for 15 min in an environment where air had been evacuated by repeated use of N<sub>2</sub> gas. Before heating, the pressure of the N<sub>2</sub> protective gas was also set to 6 bar above atmospheric. Following this, the reactor was cooled down to 110 °C, at which 15 bars over pressure of CO<sub>2</sub> was added to the reactor. The reactor was then let stir until the CO<sub>2</sub> gas was consumed. After CO<sub>2</sub> depletion, the stirring was turned off and left at 110 °C for 30 min, in order to enable two phases to form. The reactor was then let cool to about room temperature before disassembling. The lighter phase was either kept for analysis or discarded, while the heavier lignin rich phase is left to dry and subsequently extracted and kept as a powder.

#### 3.1.2 POLO

Before initiating POLO, a fieldtrip to the plant at SunCarbon in Piteå was made. Based on what was learned at the fieldtrip and after adapting the process to available conditions and equipment at Tygelsjö, the lignin powder previously made was treated according to the following.

##### 3.1.2.1 Step 1

First lignin was pestled and mixed with a sulfuric acid solution. The solution was then centrifuged until a clear solution and a solid like substance was obtained. The clear solution was discarded while the solid was kept. Step 1 was then repeated two additional times.

##### 3.1.2.2 Step 2

The lignin was mixed with deionized water and then filtrated by vacuum filtration and left to dry.

##### 3.1.2.3 Step 3

Methanol, water, H<sub>2</sub>SO<sub>4</sub> and acetone was mixed.

Lignin was pestled and slowly added under heating and stirring, until a homogenic solution was obtained. The solution was then treated with water and cooled, which made the lignin precipitate. The solid was kept for further treatment.

#### 3.1.2.4 Step 4.

Lastly, the lignin was pestled and mixed with deionized water and filtered.

In order to make a suitable amount of lignin for further experiments, the procedures of base catalysis, SOLO and POLO step 1-3 were repeated several times.



Figure 8. Equipment used for POLO from left to right. 1: Water bath. 2: Mantled glass reactor with the bottom part being connected to 1 for heating and the top part being used for cooling of fumes. 3: Centrifuge. 4: Vacuum filter flask with Buchner funnel on top.

The yield of the POLO procedure was calculated according to equation 1.

$$\text{Yield}(\text{Lignin, POLO Step 3}) = \frac{\text{Amount after}}{\text{Amount before}} \quad (1)$$

### 3.1.3 Feed mixing

To remove sample variation in the upcoming catalytic hydrotreatments, a bulk of lignin and VGO was made according to the following. The previously made lignin samples were dried and pestled. A water/acetone mixture was added to a beaker. The surfactant was then added to the water/acetone with a weight of 5 % of the dried lignin weight. Then the mixture was heated and stirred, using a magnetic stirrer, in a water bath. The lignin was dissolved by slowly adding it to the mixture. Additional acetone was also added to increase solubility. VGO which was preheated to the same temperature as the mixture was then added. The temperature was then slowly increased to 92 °C over a span of several hours. As the temperature increased, water and acetone evaporated, and the boiling point of the solution increased as well. Furthermore, as the acetone and water evaporated the lignin started to precipitate slowly which caused a fine suspension to be formed. The lignin suspension was then cooled down to 40-50 °C before being slowly mixed with additional VGO.

## 3.2 Catalytic hydrotreatment of lignin

This section contains the focus of this thesis, which is the catalytic hydrotreatment of lignin as well as the selected design of experiments.

### 3.2.1 Design of experiments

Due to limitations in material, time, lengthy production steps and several leaks, the design of experiments for the evaluation of catalytic hydrotreatment of lignin were selected to be conducted by a central composite design. The central composite design was set by the software Design expert 11 by setting lower and upper limits as well as total number of experiments possible. The parameters chosen as well as the lower and upper limit were based on the results of the method development, which is found in section 5.2.1. The design ended up having 2 factors, 8 non-centre points and 2 centre points which were also used to verify the method of analysis. The design is shown in Figure 9 while the parameters as well as the added amounts of reactants are presented in Table 1. Important notification is that the experiments ending with .1 contains lignin. For example, MEX 12.1 contains lignin, while MEX 12 does not. However, both experiments have identical parameter setting of treating time and H<sub>2</sub> pressure.

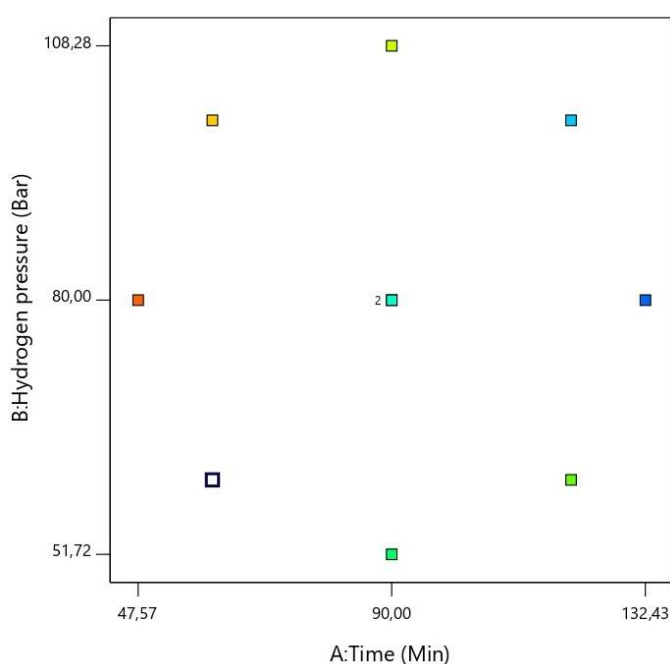


Figure 9. Central composite design generated by the software Design Expert 11.

Table 1. Showing parameters set by the central composite design as well as the amounts inserted in each experiment. H<sub>2</sub> calculated by ideal gas law

Sample	Time (min)	H <sub>2</sub> pressure (bar)	H <sub>2</sub> (g)	VGO or VGO/lignin (g)	Total mass in (g)
MEX 7	60.0	101.7	2.95	150.4	155.8
MEX 7.1	60.0	100.1	2.90	151.8	157.2
MEX 8	120.0	100.0	2.90	152.0	157.4
MEX 8.1	120.0	99.3	2.88	150.4	155.8
MEX 9	90.0	80.9	2.34	150.6	155.4
MEX 9.1	90.0	80.4	2.33	150.2	155.0
MEX 10	132.0	80.2	2.32	150.2	155.0
MEX 10.1	132.0	80.0	2.32	150.6	155.4
MEX 11	60.0	60.0	1.74	150.8	155.0
MEX 11.1	60.0	60.2	1.74	150.4	154.6
MEX 12	90.0	51.5	1.49	150.2	154.2
MEX 12.1	90.0	51.5	1.49	150.8	154.8

<b>MEX 13</b>	90.0	80.0	2.32	151.2	156.0
<b>MEX 13.1</b>	90.0	81.5	2.36	150.2	155.1
<b>MEX 14</b>	47.5	80.0	2.32	151.0	155.8
<b>MEX 14.1</b>	47.5	80.0	2.32	150.2	155.0
<b>MEX 15</b>	120.0	60.6	1.76	150.4	154.7
<b>MEX 15.1</b>	120.0	60.4	1.75	150.8	155.0
<b>MEX 16</b>	90.0	107.6	3.12	146.6	152.2
<b>MEX 16.1</b>	90.0	107.9	3.13	150.0	155.6

### 3.2.2 Experiments

For each experiment with lignin there was also one experiment carried out without lignin, which served as a reference for the analysis. Each run was carried out by having 150 g of either VGO or VGO/lignin mixture as well as 2.5 g pre-sulphated NiMo catalyst HDC-10 which was supplied by SunCarbon. This was placed in a Parr 4570 series reactor, setup in Figure 10. To remove O<sub>2</sub> from the reactor it was then flushed with N<sub>2</sub>. Subsequently it was filled with H<sub>2</sub> to a pressure of 60-150 bar at room temperature. The reactor was then heated to 325-480 °C. During heating it was stirred at 300 rpm. As the target temperature was reached, the stirring was increased to 1,050 rpm. The reactor was then kept at the target temperature for 30-240 min. The reactor was subsequently cooled down to at least 30 °C before opening. In most instances, it was left to cool over night to room temperature. The gas was then treated through an active carbon filter before being discarded. Furthermore, to remove possibly solved H<sub>2</sub>, the reactor was flushed with N<sub>2</sub>. The contents of the reactor were then filtered (Macherey-Nagel MN 713 Ø 70mm) to separate the product from the catalyst.

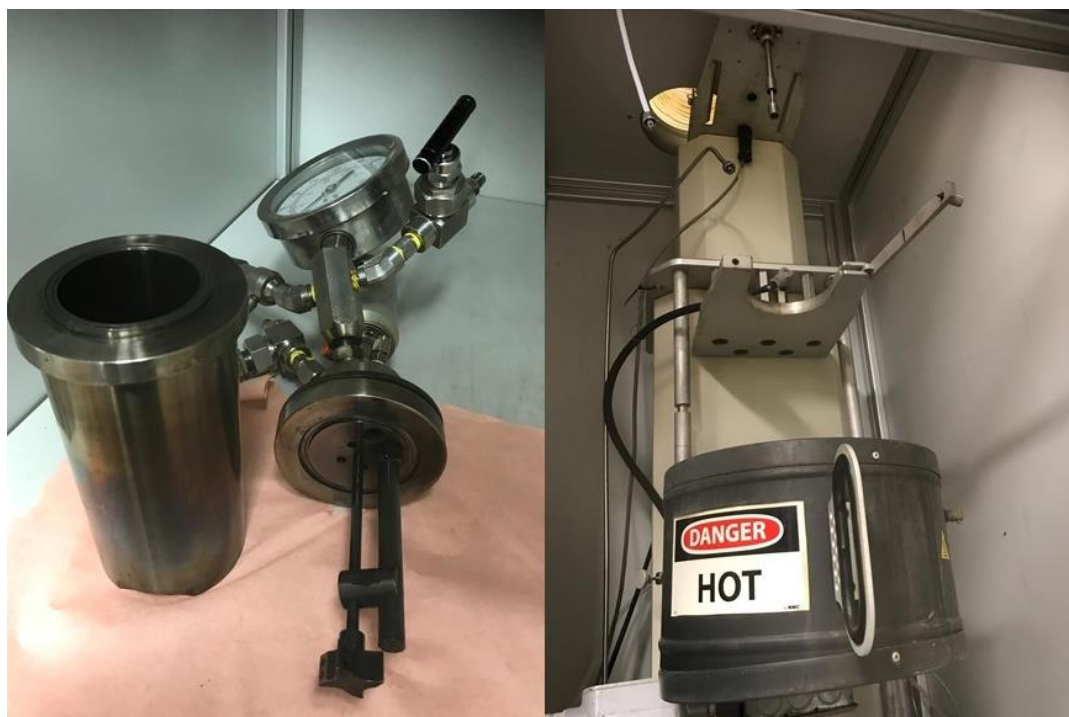


Figure 10. Left picture showing the reactor bottom and top which the materials were placed in. Right picture showing the construction where the reactor was placed and utilized.

### 3.2.3 Mass balances

The yields of liquid were calculated by having the weight of the liquid obtained after filtration, divided by the total mass of reactants in each experiment. The yields of gas were measured by weighing the reactor prior to and then after each experiment, divided by the mass of reactants in each experiment, after the evacuation of gas. The values regarding coke are based on the following equation 2:

$$Coke_{after}(g) = Total\ mass_{before}(g) - Gas\ vented_{after}(g) - filtered\ liquid_{after}(g) \quad (2)$$

The coke was then divided by total mass of reactants. The main issue with this equation is that most likely not all filtered liquid is accounted for. This is due to liquid being bound to solid material (coke) as well as some being attached to the walls of the reactor, the beakers, the filter and in the pores of the catalyst. The coke value can therefore be regarded as a worst-case value. However, since all experiments were handled the same way afterwards, they still represent a good value for comparison in-between samples.

The difference of coke formed between the experiments with and without lignin were compared according to equation 3 and 4 in order to evaluate the method and equipment.

$$Difference(g) = Coke_{Lignin\ experiment}(g) - Coke_{VGO\ only\ experiment}(g) \quad (3)$$

$$Difference\ to\ mass\ in\ (w\%) = \frac{Difference(g)}{Total\ mass\ in\ (g)} \quad (4)$$

## 3.3 Analysis

In this section the analysis used is presented. Furthermore, the results in the following sections were analysed using the Design Expert 11 software.

### 3.3.1 GC-FID

For the analysis, a gas chromatography with a flame ionization detector (GC-FID) was used to evaluate the results after hydrotreating. The GC-FID used was a Varian CP-3900 with a 1177 injector and FID detector. The column specification was 15 m, 0,25 mmID, 025 um and BR-1ms.

The GC-FID evaluation was conducted according to the following: Gasoline bought at a gas station, and biodiesel which were made and provided by Hulteberg Chemistry & Engineering AB, were analysed to see at what times that most of the gasoline and diesel molecules were ejected from the GC column. These time values were then used as the upper and lower limits for integration of the hydrotreated samples. The hydrotreated samples were then injected into the GC-FID, after which the area of the selected intervals is divided by the total area for the whole sample, equation 3.

$$\alpha = Indicative\ values\ of\ diesel\ and\ gasoline\ fractions = \frac{\int_{Lower,diesel}^{Upper,diesel} Sample}{\int_{-\infty}^{\infty} Sample} \quad (3)$$

The value  $\alpha$  is then a measurement which can be compared to other samples which have different parameter settings.

### 3.3.2 ICP-OES

To examine the extent to which the POLO wash was effective in producing lignin with a low metal content, samples were taken before, during and after POLO. The samples were then dried in an oven at 105 °C at 24 h before being sent to SunCarbon in Piteå for ICP-OES analysis. The ICP-OES used was a Perikin and Elmer 200 equipped with a Perkin Elmer S10 autosampler.

## 4 Results and discussion

This section presents and discusses the results from the experiments as well as the analysis.

### 4.1 Pre-treatment

In this section, the results of POLO are shown and analysed. Due to time limitation as well as being out of scope of aim, base catalysis and SOLO were not analysed.

#### 4.1.1 POLO

During POLO, there were some losses of lignin in each step. Step 1 ( $\text{H}_2\text{SO}_4$  wash followed by centrifugation) showed only minor losses as indicated by the transparent solution in Figure 11.

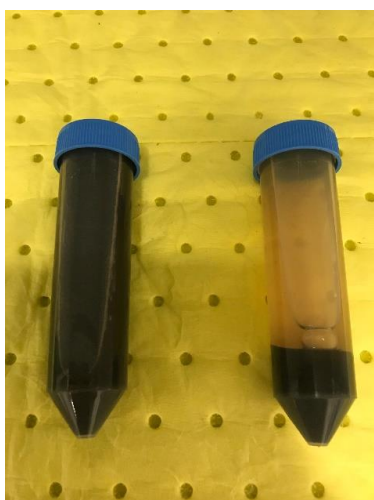


Figure 11. Before (left) and after (right) centrifugation. Right: The transparent solution at the top was discarded, while bottom solid was kept.

However, when it came to step 3 several issues arose. When trying to solve lignin (34.2 g) without the addition of acetone, there were difficulties in solving the lignin. When adding the dried powder into solution, it instantly formed a large solid/smelt like substance as seen in Figure 12. The solid/smelt substance was then picked up with a pair of tweezers and pestled and dried before being added to the solution again. However, the solid/smelt substance kept on forming without showing noticeable decrease in size.



Figure 12. Unsolved lignin picked up by tweezers to be pestles before added to solution.

Acetone (50-200 ml) was thus added before the addition of the lignin. This led to no noticeable solid/smelt substance being formed. Instead the solution was noticeably darkened by the addition of lignin. The first acetone attempt had a of temperature 58-60 °C which was apparently too high, seeing as the solution level kept decreasing. This assumedly indicated that acetone had evaporated which made it hard to determine how much acetone was in the solution at a given time.

Continuing after the first attempt, the temperature was lowered to 50 °C and 200 ml of acetone was added. Furthermore, the amount of lignin in each wash was increased to 60-100g per wash. Even with the added amount of lignin there were no further issues regarding the solvability of lignin.

Another concern was the losses in Step 3. By examining the yield in equation 2. The yield was only 57.1%.

$$Yield(Lignin, POLO Step 3) = \frac{225,1 g}{394,0 g} = 0,571 \quad (1)$$

This means that 42.9 % of the lignin was simply washed off along with the discarded solution. To examine the procedure, the discarded solution was left to cool/rest after which it was carefully poured into another beaker. The previous beaker showed a minimal additional amount of precipitated lignin. To the beaker still containing the discarded solution, an equal amount of deionized water was added and left to rest. Coming back several hours later and carefully pouring the discarded solution mixed with water into another beaker showed a large amount of lignin in the bottom. This showed that a lot of the lignin were still in the discarded solution, as indicated by the previously mentioned yield calculation.

The results from the ICP-OES analysis is presented in **Fel! Hittar inte referenskölla..**

Table 2. ICP-OES averages data results. ICP-OES tests and data supplied by Daniela Rusanova Naydenova at SunCarbon. All data available in appendix

Labels	Al 394.40 (ppm)	As 193.69 (ppm)	Ba 233.53 (ppm)	Ca 317.93 (ppm)	Cd 214.44 (ppm)	Cr 284.33 (ppm)	Cu 327.39 (ppm)
<b>After POLO</b>	84.07	< 0.1	5.02	7.79	< 0.1	107.05	1.33
<b>Prewash</b>	79.05	< 0.1	3.54	13.30	0.08	124.77	0.81
<b>Before POLO</b>	148.08	< 0.1	8.08	892.90	0.30	97.91	1.00
Labels	Fe 238.20 (ppm)	K 766.49 (ppm)	Mg 285.21 (ppm)	Mo 202.03 (ppm)	Mn 257.61 (ppm)	Na 589.59 (ppm)	Ni 231.60 (ppm)
<b>After POLO</b>	26.46	2.46	5.05	38.96	0.82	4.80	29.48
<b>Prewash</b>	44.30	15.21	7.53	27.85	4.71	53.80	23.73
<b>Before POLO</b>	84.05	5444.15	330.46	23.31	170.18	36727.67	52.66
Labels	P 213.62 (ppm)	Pb 220.35 (ppm)	Si 251.61 (ppm)	Sr 421.55 (ppm)	Ti 334.94 (ppm)	V 292.46 (ppm)	Zn 213.86 (ppm)
<b>After POLO</b>	1.41	< 0.1	88.05	0.10	1.78	4.97	4.52
<b>Prewash</b>	1.75	< 0.1	283.02	0.10	1.49	4.77	17.21
<b>Before POLO</b>	124.42	< 0.1	356.27	3.05	1.16	4.57	35.38

These results show that there is a large reduction in most of the metals. By looking at the content of Na, which is the most prevalent substance present before POLO, being at 36727.67 ppm. As seen, after the prewash there is 53.80 ppm remaining while after POLO there is 4,80 ppm remaining. This shows a



reduction of 99.99 %. In the case of K these values are 5444.15, 15.21 and 2.46 ppm respectively. Which indicates a reduction of 99.96 %.

The results could have been affected by the fact that the lignin powders were handled by tools made of metal. Furthermore, since the experimental hall is utilized to produce various catalysts containing metals, it is possible that minor amounts of dust has been affecting the results.

#### 4.1.2 Feed mixing

The lignin suspension was of 455 g before final lignin/VGO mixture. Since the lignin, surfactant and VGO added had a total weight of 461.1 g initially. This indicates a minor loss of 1,3 %. Which is quite good considering that the solution was kept at elevated temperature for several hours. Figure 13 below shows the various stages performed of the sample homogenization.



Figure 13. The pictures from left to right shows the proceedings of the sample homogenization. Left: Lignin has been dissolved into acetone/water/surfactant mixture. Middle left: Mixture of lignin/acetone/water/surfactant/VGO at boiling point around 52-92 °C Middle right: Mixture of lignin/surfactant/VGO round 92 °C Right: Lignin/surfactant/VGO mixture mixed with a larger bulk of VGO, about 10 w% lignin.

## 4.2 Catalytic hydrotreatment of lignin

In this section the catalytic hydrotreatment experiment results and method development are presented.

### 4.2.1 Method development

The parameters for the initial six experiments of the method development can be seen in Table 3 below.

Table 3. Experiments conducted for the method development. Samples MEX 1-6, they set parameters as well as product comments.

Sample name	Temperature (°C)	H <sub>2</sub> Pressure (Bar)	Time (Min)	Product comments
MEX 1	325	90	60	No hydrogen consumption.
MEX 2	400	90	90	Unsuccessful filtration. Low hydrogen consumption. Semi solid in fridge.
MEX 3	420	100	240	Successful filtration. Semi solid in fridge.
MEX 4	420	100	360	Successful filtration. Semi solid in fridge.
MEX 5	420	100	180	Successful filtration. Semi solid in fridge.
MEX 6*	480(410-480)	100	90-120	Successful filtration. Remains liquid in fridge. Basis for continued experiments.

Due to limited amounts of lignin as well as a bulk consisting of 90 w% VGO, the first two trials were conducted on VGO and catalyst only. The first two experiments, MEX 1 and MEX 2 respectively, failed with little or no consumption of H<sub>2</sub>. Presumably due to insufficient time or temperature. The resulting products had characteristics similar to untreated VGO, and it was unfilterable.

For the experiments of MEX 3-5, the temperature was increased to 420 °C and the H<sub>2</sub> pressure increased to a 100 Bar. Experiments were then conducted with varying durations (180, 240 and 360 min) at the target temperature. The resulting products were filterable, and the duration of filtration was closely related to the harshness of treatment, with harsher treatment leading to faster filtration. By looking at and comparing the samples it was clear that reactions had occurred. The extent to which the sample had reacted seemed closely related to the duration, as shown in Figure 14.

During the experiment of MEX 6, as the temperature was getting close to 460 °C the pressure started to increase faster than the previous somewhat linear increase. Furthermore, the temperature started to level out, even though the heater was heating at 100% since it had not yet reached the target of 480 °C. This indicated that endothermic reactions were becoming dominant in the reactor. Due to the temperature levelling out, it was decided that it was the moment that would be the starting point in time of the experiment. Thus, the stirring rate was increased from 300 rpm to 1050 rpm. Following the increase of stirring rate, the temperature dropped from 460 °C down to 420-430 °C. It was also noted that the heater could not keep up with the endothermic reaction, for about 60-90 min. Examples of how the pressure and temperature profiles changed during the experiments are shown in Figure 16 and Figure 17. Unfortunately, a water pipe broke somewhere in the treatment time of 60-120 min. The leakage resulted in a circuit breaker being triggered. This in turn led to the loss of data for the experiment. However, even though it is unknown exactly how long the treatment lasted, it had continued for at least an hour and the reactor was still sealed and pressurized. Thus, even though there were some irregularities, the experiment was still considered useful. Upon examining the contents of the reactor. The product was very easily filtered, and it was of a dark red colour, see MEX 6 in Figure 14.



Figure 14. From left to right: Untreated VGO, MEX 1, MEX 5, MEX 3, MEX 4, MEX 6. The ordering of MEX 5, 3 and 4 is by increased time.

Upon storing all previous samples in the fridge, it was discovered that most samples semi-solidified. It was also noticed that the untreated VGO semi-solidified as well. The only exception was MEX 6, which showed no indication of solidifying, Figure 15.



Figure 15. From left to right. V60, MEX 5, MEX 3, MEX 6 and MEX 6. The samples have just been taken out from the fridge and all except for MEX 6 shows semi-solid behaviour.

The non-solidification of MEX 6 during storage in the fridge indicates that smaller carbon molecules were present in the products, and thus hydrocracking had assumedly happened to some extent. Since the purpose of the thesis is the production of petrol and diesel, the continued experiments were decided to be conducted using the temperature settings of MEX 6, because, it showed no sign of solidifying.

The method development thus ended with the temperature for all the following experiments being set to a fixed setting with a target of 480 °C. The parameters that would be examined in closer detail were those of time and H<sub>2</sub> pressure.

## 4.2.2 Hydrotreatment experiments

In this section, the results of the hydrotreatment experiments are discussed and presented. Important notice is that the experiments ending with .1 contains lignin. For example, MEX 12.1 contains lignin, while MEX 12 does not. However, both experiments have identical parameter setting of treating time and H<sub>2</sub> pressure.

### 4.2.2.1 Experimental deviations

It should be noted that in experiment MEX 8.1 the stirring rate increase from 300 rpm to 1,050 rpm was forgotten for the first 30 min on the experiment (120 min total). However, upon increase, the temperature did not fall much nor did the pressure change as much as it had during previous experiments. Thus, it is assumed that the 30 min deviation of rpm did not affect the results that much.

Experiment MEX 10.1 had to be aborted about 10 minutes before the completion of the 132 min experiment, by turning off the heater. The reason was that the pressure was at 307 bars, while at an increase of 3-4 bar per min. Therefore, there was a risk of breaking one of the security measures and reaching the limit of pressure tolerance of the equipment, which is set at around 340 bar. To reduce the impact of the shortened experimental time, cooling was not initiated as it normally would be. Instead, the heater was kept at heating position, which leads to a slower cooling. This is shown in Figure 16.

### 4.2.2.2 Temperature & pressure profiles

In order to examine differences between lignin and non-lignin experiments, the temperature profiles of a few experiments are presented in Figure 16 and Figure 17.

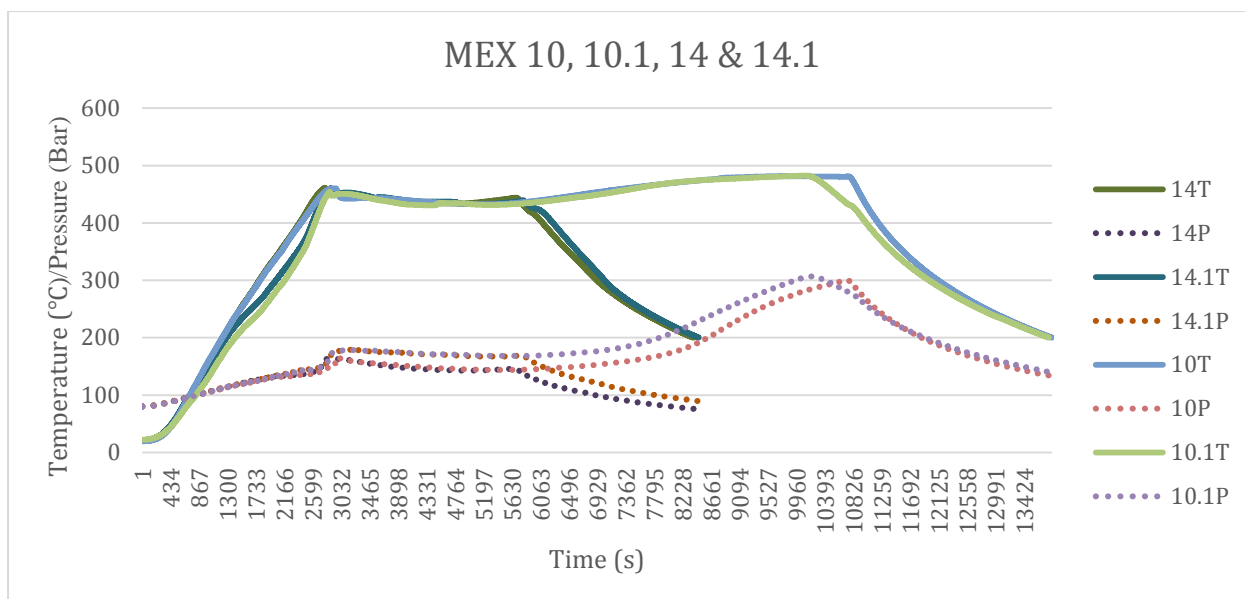


Figure 16. Temperature and pressure profiles for MEX 10, 10.1, 14 and 14.1. All 4 experiment were carried out at the same starting  $H_2$  pressure of 80 bar, while time was the varying parameter. MEX 10 and 10.1 was treated for 132 min, while MEX 14 and 14.1 were treated for 47 min.

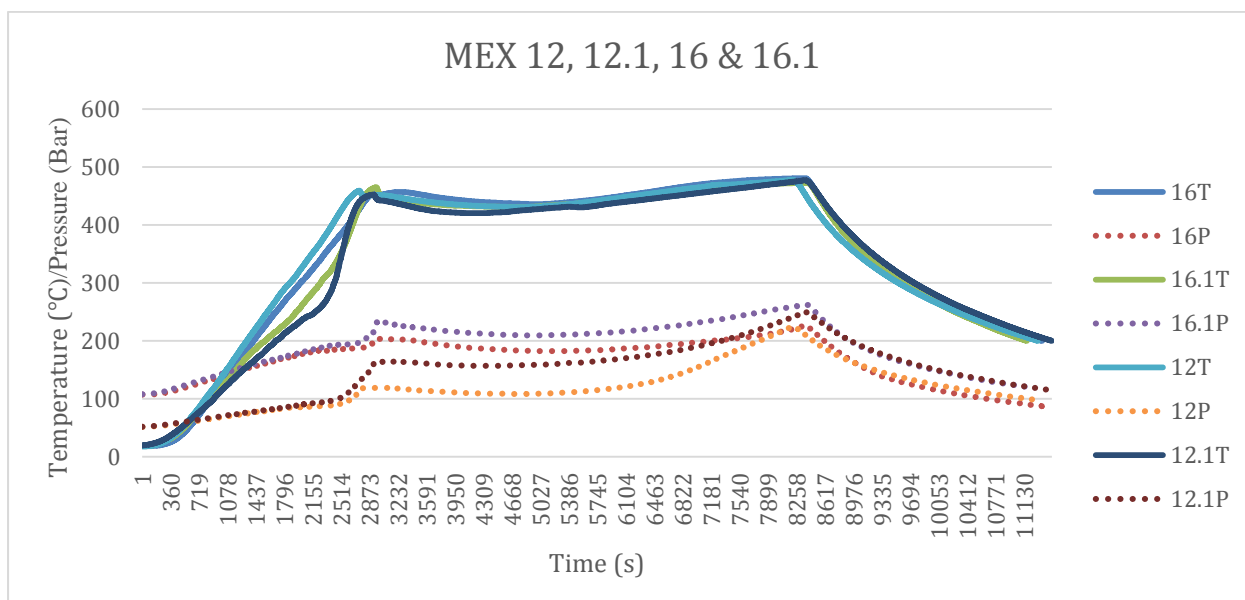


Figure 17. Temperature and pressure profiles for MEX 12, 12.1, 16 and 16.1. All 4 experiment were treated for the same time duration of 90 min, while starting  $H_2$  pressure was the varying parameter. MEX 12 and 12.1 had a starting  $H_2$  pressure of about 51 bar while MEX 16 and 16.1 had a starting pressure of about 108 bar.

During the heating phases (of about 1-2,900 s) there is a large difference in the temperature profile for the experiments with the lignin. The slope seemingly does not increase as much at first compared to the non-lignin experiments, only to pick up the pace later. A possible cause could be that there are more endothermal reactions happening at lower temperatures in the experiments with lignin. Another possibility is that the water present in the lignin samples evaporated at those pressures and temperatures. Thus, absorbing heat, since there was assumedly water droplets were detected following several lignin experiments (Figure 18).



Figure 18. Assumed water droplets found after filtrating the liquid content in the reactor following experiment containing lignin mixture.

As depicted in Figure 16 and 17, the heating phase ends by a sharp spike in pressure as well as a decrease in temperature. This is due to the stirring being increased from 300 to 1050 rpm, which enables more interaction between  $H_2$  and the other substances, as well as better heat transfer. As the reactions proceed the temperature and pressure decreases. For the experiments that were longer than about an hour, the temperature and pressure started to rise again. It seems that at this point the endothermic reactions starts to slow down, possibly due to coke formation on the catalyst, less hydrocarbons available for reactions, or the depletion of  $H_2$ . However, this is hard to determine without sampling at various stages in the experiment.

Each run ends by a cooling phase, which were significant decreases in both temperature and pressure. The general trend seemed to be that the experiments with lignin ended up at a higher pressure. Both at the end-of-the-run time, but also at the end of the shown cooling time (at 200 °C). Interestingly enough, looking at Figure 17, what can be seen is that MEX 12 + 16 and 12.1 + 16.1 ends up at similar pressures toward the end of the run, even though they had different amounts of  $H_2$ . In order to explain thus, further investigation is required.

#### 4.2.2.3 Mass balances

The results of the mass balances are summarized in Table 4.

Table 4. Yields of coke, gas, liquid as well as the parameters of time and  $H_2$  pressure for each experiment. The sample notification ending with 1 indicates an experiment with 10w% lignin.

Sample	Time (min)	$H_2$ pressure (bar)	Coke (w%)	Gas after(w%)	Liquid(w%)
MEX 7	60.0	101.7	9.1	10.4	78.9
MEX 7.1	60.0	100.1	10.8	15.0	72.6
MEX 8	120.0	100.0	13.8	40.7	44.0
MEX 8.1	120.0	99.3	21.1	32.4	44.9
MEX 9	90.0	80.9	10.0	29.7	58.7
MEX 9.1	90.0	80.4	11.2	21.5	65.7
MEX 10	132.0	80.2	22.4	34.8	41.2
MEX 10.1	132.0	80.0	25.9	39.4	33.1

MEX 11	60.0	60.0	6.8	15.5	76.1
MEX 11.1	60.0	60.2	15.1	16.2	67.1
MEX 12	90.0	51.5	13.5	25.5	59.4
MEX 12.1	90.0	51.5	23.3	27.3	47.8
MEX 13	90.0	80.0	10.1	20.5	67.8
MEX 13.1	90.0	81.5	21.9	24.4	52.1
MEX 14	47.5	80.0	5.6	10.4	82.4
MEX 14.1	47.5	80.0	9.6	11.4	77.4
MEX 15	120.0	60.6	14.5	33.1	50.8
MEX 15.1	120.0	60.4	29.5	38.4	30.4
MEX 16	90.0	107.6	6.1	25.9	66.4
MEX 16.1	90.0	107.9	11.1	24.2	63.1

By looking at Table 4, what can be seen is that the best experiments, with the least coke and the most liquid, are experiments 7.1 and 14.1 for lignin. Those experiments were carried out with medium to high amounts of H<sub>2</sub> and with low process time, section 5.3. The highest formation of coke was seen in the experiments of 10.1 and 15.1, which were carried out at medium to low H<sub>2</sub> pressure and at long time duration.

To gain an overview of how the parameters affected the yields, the data of Table were inserted and analysed in Design Expert 11. The results are shown in Figure 19, Figure 20, Figure 21 as well as in the regression analysis in the appendix.

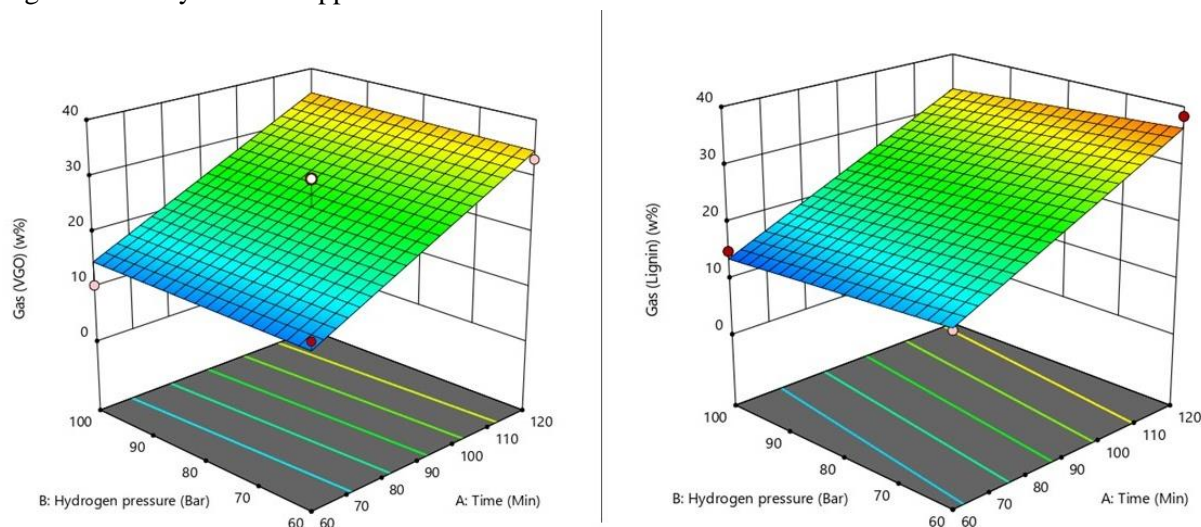


Figure 19. Central composite design results showing how the parameters of initial H<sub>2</sub> pressure and reaction time affected the gas (w%) evacuated after each experiment after cooling. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design Expert 11 and later modified for easier comparison. Red and white dots show the data points from the experiments.

By looking at Figure 19 what can be seen is that the VGO experiments show that reaction time heavily affect the amount of gas produced, while the content of H<sub>2</sub> had no effect on the results. This indicates that the amount of H<sub>2</sub> was above what was needed in all the VGO experiments for all experiments. Looking at the lignin experiments, what can be seen is a time dependency, just as with the VGO experiment. Furthermore, the lignin experiments also show a trend in the H<sub>2</sub> content, an increase in H<sub>2</sub> leads to a lower amount of gas losses.

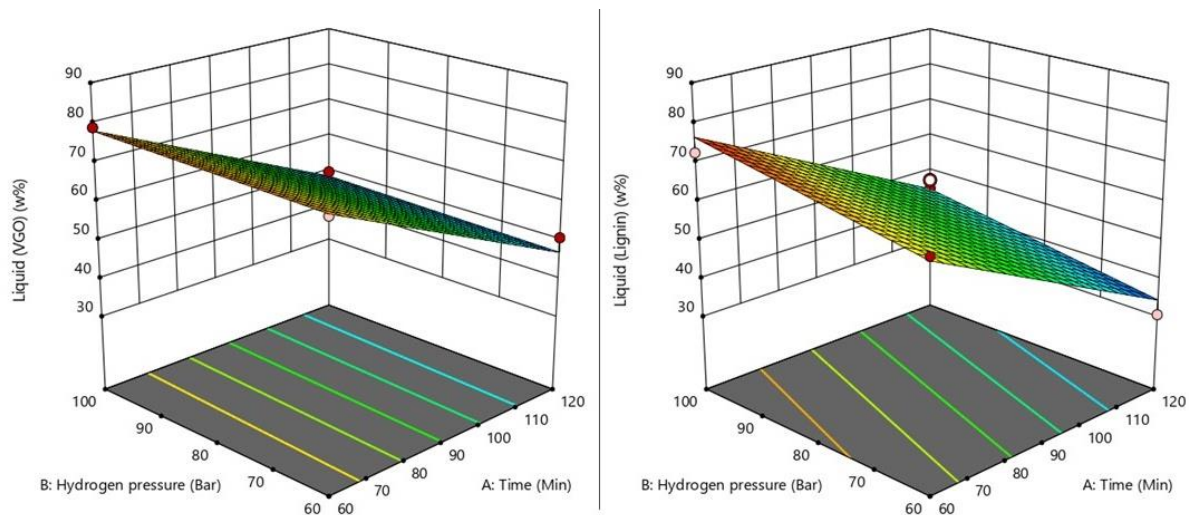


Figure 20. Central composite design results showing how the parameters of initial  $H_2$  and time affect the yield of liquid product. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design expert 11 and later modified for easier comparison. Red and white dots show the data points from the experiments.

Figure 20 shows that the amount of liquid obtained is reduced as time progresses. Moreover, the lignin experiments show a clearer trend of more  $H_2$  resulting in more liquid, in comparison to the VGO only experiments.

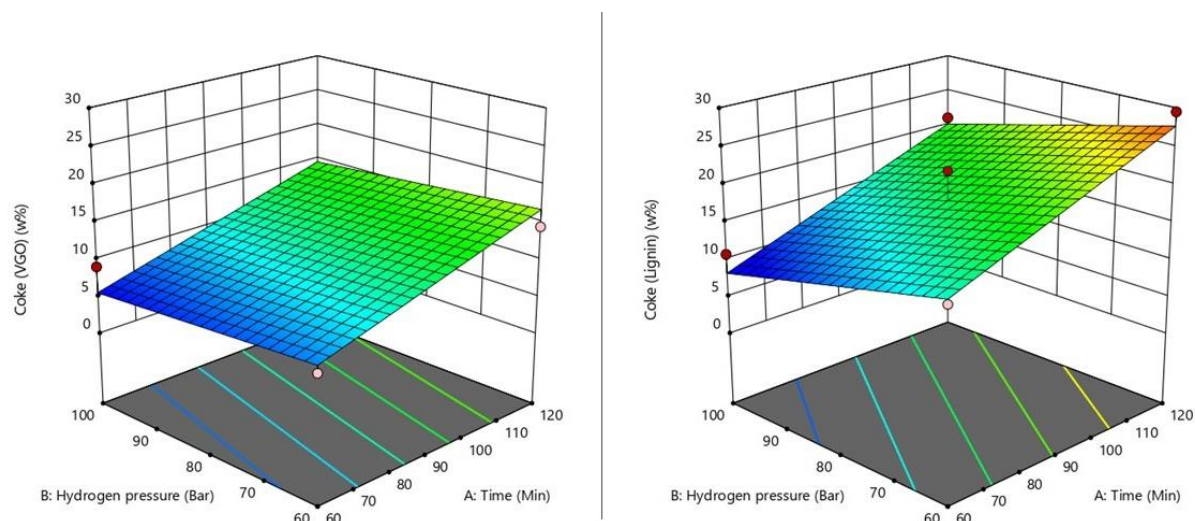


Figure 21. Central composite design results showing how the parameters of initial  $H_2$  and time affect coke formation. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design expert 11 and later modified for easier comparison. Red and white dots show the data points from the experiments.

The values of Figure 21 are derived from mass balances containing 4 parts, material in, gas out, liquid out and coke out. Since the first three are measured, it follows that the rest of the w% will be that of coke. However, the faults of measuring the first three will be present in the calculated forth. Furthermore, the formation of coke in the lignin experiments were all higher than those of the VGO experiments, with a clear correspondence to the duration of the experiments but also to the amount of  $H_2$  present.

To corroborate the calculated results in Figure 21, Figure 22 shows that a lot more coke was formed in the experiments of MEX 13.1 and 14.1 containing lignin, in comparison to the non-lignin of MEX 13 and 14.



Figure 22. Picture showing coke found in the reactor after the following experiments from left to right: MEX13, MEX13.1, MEX 14 and MEX14.1 The pictures shows that a lot more coke was found in the lignin experiments upon opening of the reactor.

Since more coke was formed in the lignin experiments, it could be that a lot of the lignin was mostly turned into coke. To further examine the difference in the amount of coke ( $\text{Coke}_{\text{Lignin}}(\text{g}) - \text{Coke}_{\text{VGO}}(\text{g})$ ) as well as how that amount relates to initial mass, the following table 5 was set up.

Table 5. Table showing the calculated difference of coke of samples with lignin – samples without(g). The column to the right show how the coke difference relates to the total mass I each sample (w%). All experiments show more coke in the lignin samples.

Sample	Coke difference (g)	Coke difference (w%)
MEX 7	2.75	1.81
MEX 7.1		
MEX 8	11.18	7.43
MEX 8.1		
MEX 9	1.79	1.19
MEX 9.1		
MEX 10	5.59	3.71
MEX 10.1		
MEX 11	12.81	8.51
MEX 11.1		
MEX 12	15.30	10.15
MEX 12.1		
MEX 13	18.24	12.15
MEX 13.1		
MEX 14	6.20	4.13
MEX 14.1		
MEX 15	23.39	15.51
MEX 15.1		
MEX 16	8.01	5.34
MEX 16.1		

Table 5 shows that the experiments with medium to lowest amount of  $\text{H}_2$  (MEX 11, 12, 13 and 15) are those with the highest difference in the amount of coke. To show the relationship of coke difference more clearly, Figure 23 was made by inserting the values of w% in Table 5.



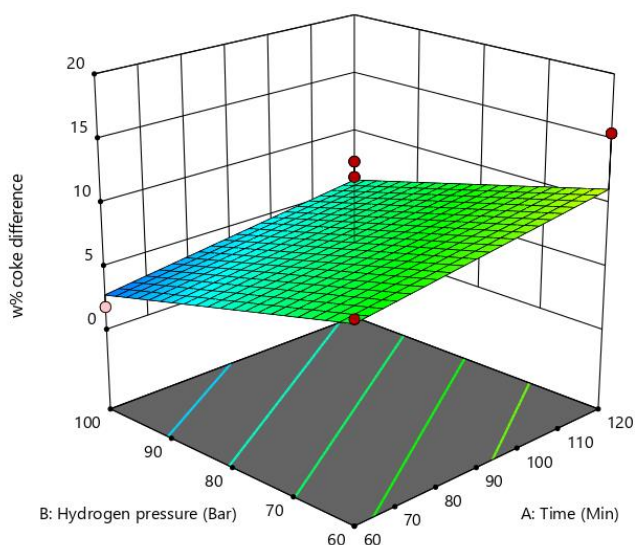


Figure 23. Figure based on data in Table 5, indicating a difference in coke between lignin and non-lignin experiments. Red and while dots show the data points from the experiments.

By examining Figure 23 there is a clear trend, which indicates that the smaller the coke difference the less time and more of H<sub>2</sub> that were present in the experiments. This could indicate that lignin is more prone to coke formation with lesser H<sub>2</sub> present. However, it cannot be concluded with certainty given that the coke formation is calculated and that only a few of the experiments were repeated. Furthermore, the lignin samples had 10 w% lignin, and several samples showed close to or above 10 w% coke difference. This means that there is a possibility that all the lignin in those samples turned into coke. Thus, there is a possibility of no yield of gasoline or diesel from lignin in those samples in the following sections of GC-Fid and overall evaluation.

#### 4.2.2.4 GC-FID

Three example chromatograms are shown below for gasoline, diesel and one experiment.

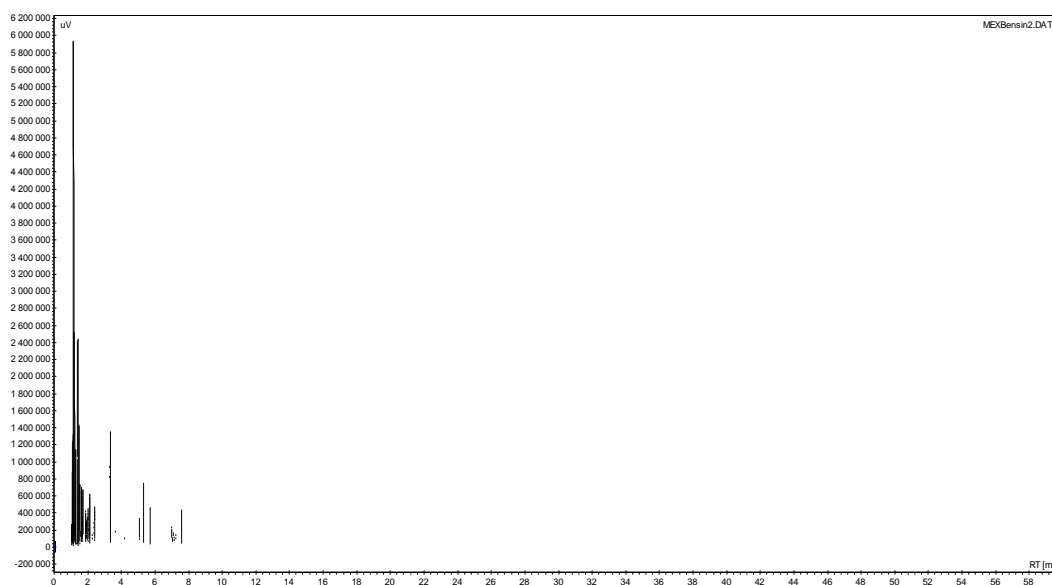


Figure 24. GC-Fid chromatogram of commercial gasoline bought at a local gas station. Made by utilizing CompassCDS.

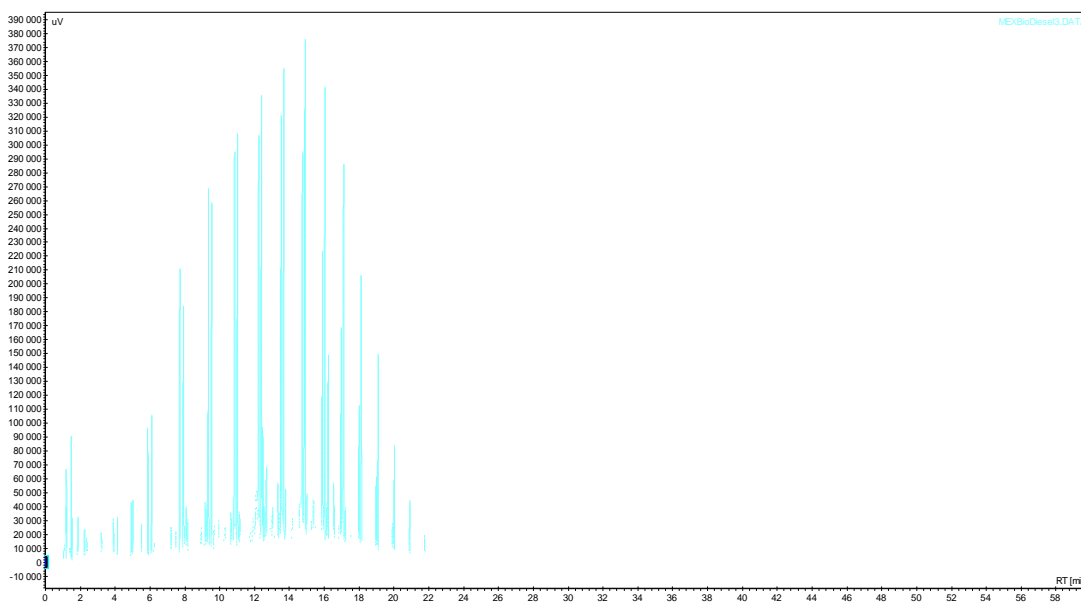


Figure 25. GC-Fid chromatogram of biodiesel made and provided by Hulteberg. Made by utilizing CompassCDS.

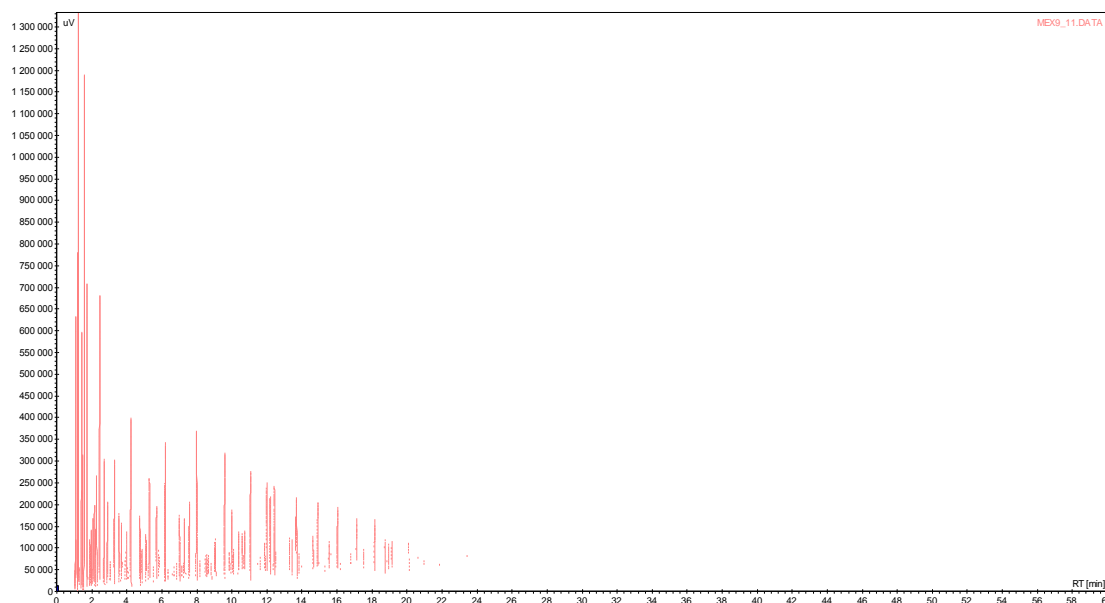


Figure 26. GC-Fid chromatogram of MEX 9.1. Made by utilizing CompassCDS.

While analysing the data of gasoline and diesel, it was found that 96.3 % and 86.4 % of the substances were found in the intervals at 0-8 min and at 8-20 min respectively. The intervals were then selected as a way of determining the assumed quantity of the carbon molecules present for the experimental data.

#### 4.2.2.5 Overall evaluation

The areas for all experiments as well as the corresponding yield of relevant carbon molecules are presented in Table 6.

Table 6. Data showing the area/total area (%) for the selected intervals in each GC-Fid analysis. Moreover, data also shows how each interval correlates to total yield of relevant carbon molecules.

Sample	Area 0-8 min	Area 8-20 min	Area 0-20 min	Yield 0-8 min (w%)	Yield 8-20 min (w%)	Yield 0-20 min (w%)
Gasoline	96.3					
Diesel	11.6	86.4				
MEX 7	14.15	39.11	53.26	11.57	31.99	43.56
MEX 7.1	21.51	43.76	65.27	16.18	32.92	49.10
MEX 8	25.56	43.18	68.74	11.64	19.66	31.30
MEX 8.1	22.97	45.90	68.87	10.69	21.36	32.06
MEX 9	27.65	42.11	69.76	16.74	25.50	42.25
MEX 9.1	28.32	43.14	71.46	19.19	29.24	48.43
MEX 10	24.87	42.37	67.25	10.57	18.00	28.56
MEX 10.1	27.05	42.33	69.38	9.23	14.45	23.68
MEX 11	31.04	39.88	70.92	24.29	31.20	55.49
MEX 11.1	28.27	43.15	71.41	19.51	29.78	49.29
MEX 12	47.11	32.70	79.81	28.73	19.94	48.67
MEX 12.1	31.00	41.75	72.75	15.21	20.49	35.70
MEX 13	39.98	38.43	78.40	27.97	26.89	54.86
MEX 13.1	31.67	40.42	72.09	17.04	21.74	38.78
MEX 14	15.17	43.43	58.61	12.90	36.93	49.83
MEX 14.1	18.28	43.78	62.06	14.60	34.98	49.58
MEX 15	33.02	40.59	73.61	17.26	21.21	38.47
MEX 15.1	27.91	41.18	69.09	8.74	12.89	21.62
MEX 16	42.88	39.43	82.30	29.54	27.16	56.70
MEX 16.1	32.48	40.53	73.00	21.26	26.53	47.79

By examining the yields in Table 6 the following for each interval can be seen. Graphical representation of the yields in table 6 and the following results and discussion, is found further down in figures 30-32.

In the interval of 0-8 min, the highest yields are those of MEX 16.1, 11.1 and, 9.1, with yields of 21.3, 19.5 and 19.2 w% respectively. However, of all the yields what is noteworthy is that only MEX 14.1, 9.1 and 7.1 showed higher yields than the VGO blanks. The lowest yields were observed in MEX 10.1 and 15.1, with yields of 9.2 and 8.7 w% respectively. These results indicate a tendency for less gasoline-like molecules obtained, the longer the duration of treatments, as well as the lower the amount of H<sub>2</sub>.

In the interval of 8-20 min, the highest yields are those of MEX 7.1, 14.1 and 9.1, with yields of 32.9, 35.0 and 29.2 w% respectively. In this interval the experiments of MEX 12.1, 9.1 8.1 and 7.1 shows higher yields than the VGO blanks. The lowest yields were those of MEX 10.1 and 15.1 with yields of 14.5 and 12.9 w% respectively. These results indicate a tendency for less diesel-like molecules obtained the longer the duration of the treatments as well as the lower the amount of H<sub>2</sub>. However, there is not as clear a differentiating trend between the lignin and non-lignin results, given that the experiments with the higher yield than the blank counterpart seems more scattered in the central composite design.

Looking at the whole interval of 0-20 min, the highest yields are those of MEX 7.1, 14.1, 11.1 and 9.1, with yields 49.1, 49.6, 49.3 and 48.4 w% respectively. The lowest yields are found at MEX 10.1 and 15.1 with 23.7 and 21.6 w% respectively. Looking at the difference of lignin and non-lignin, the largest positive difference for lignin are those of 7.1 and 9.1. Those experiments differ by 5.5 (49.10-43.56) and 6.2 (48.43-42.25) w%.

Unfortunately, by looking at looking at MEX 9, 9.1, 13 and 13.1, which are set at the same parameters, what can be seen is that there is a significant difference in the results. In the interval of 0-8 min MEX 9 and 9.1 has a yield of 16.7 and 19.2 w%, while MEX 13 and 13.1 has a yield of 28.0 and 17.0 w% respectively. In the interval of 8-20 min, MEX 9 and 9.1 has a yield of 25.5 and 29.2 w%, while MEX 13 and 13.1 has a yield of 26.9 and 21.7 w% respectively. These results sum up to 42.3 and 48.4 w% for MEX 9 and 9.1, while for MEX 13 and 13.1 they sum to 54.9 and 38.8 w% respectively. This shows that for MEX 9 there is a yield increase of 6.2 w% with the addition of lignin, while for MEX 13 there is a decrease in yield of 16.1 w%. This is a clear indication that the method is overall not optimal or that something was off during the experiments.

To examine if something went wrong during the experimental procedure, the temperature and pressure profiles of identically parameter set MEX 9, 9.1, 13 and 13.1 where extracted and plotted in Figure 27 and Figure 28.

Figure 27. Temperature (9T and 13T) and pressure profiles (9P and 13P) of the non-lignin experiment of MEX 9 and 13 over a time interval of about 3 hours.

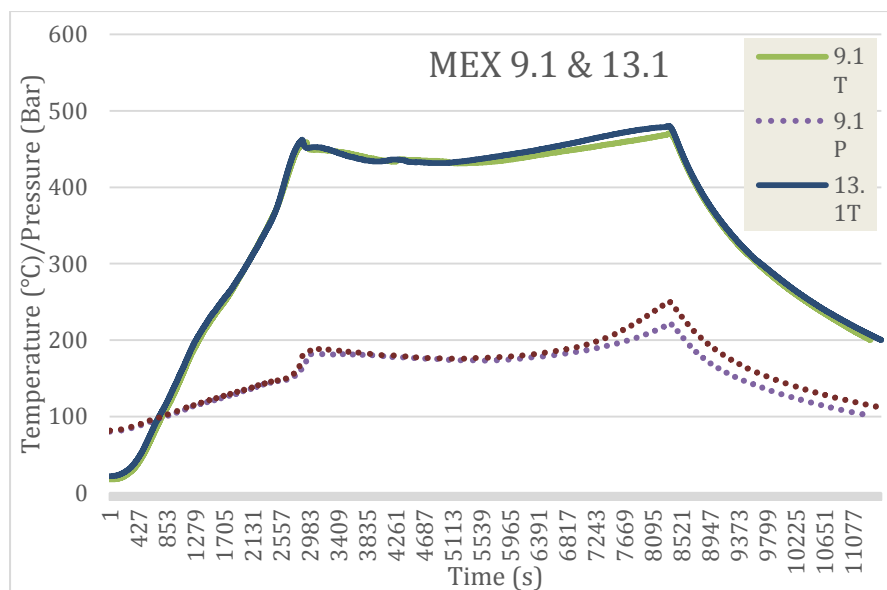


Figure 28. Temperature (9.1T and 13.1T) and pressure profiles (9.1P and 13.1P) of the lignin experiment of MEX 9.1 and 13.1 over a time interval of about 3 hours.

Looking at Figure 27 and Figure 28, what can be seen is that in both cases, after about half way into the experiment, the pressures starts differing. MEX 13.1 show higher pressures than MEX 9.1. While MEX 9 show a higher pressure than MEX 13. It is not certain why this difference of pressure arises. Possibly, it could be that there were minor leaks in the packing of the reactor. That could explain the difference, since during all experiments, the packing was replaced several times, because of damage to the packing or detected leaks, as shown in Figure 29.



Figure 29. Burnt material found outside of the reactor following an experiment.

Evidently, from these results there is a large difference between the experiments set at the same parameters. Thus, the result show that the either the equipment or method was not optimal. It could also be that too few repetitions of the experiments were set up to give reliable results, which may have caused the large variations.

MEX 9, 9.1, 13 and 13.1 had overall yields of 42.3, 48.4, 54.9 and 38.8 w%. These values show variations of 12.6 w% for the non-lignin experiments and 9.6 w% for the lignin added experiments. It is important to notice that these variations are not as large as the overall difference of yields for the non-lignin and lignin added experiments, which had variations of 28.1 (56.7-28.6 w%) and 28.0 w% (49.6-21,6 w%) respectively. Thus, the results should still overall be useful as a general direction for future work.

Continuing, by inserting the data for the yields in Table into Design Expert 11, the graphs of Figure 30, Figure 31 and Figure 32 were constructed.

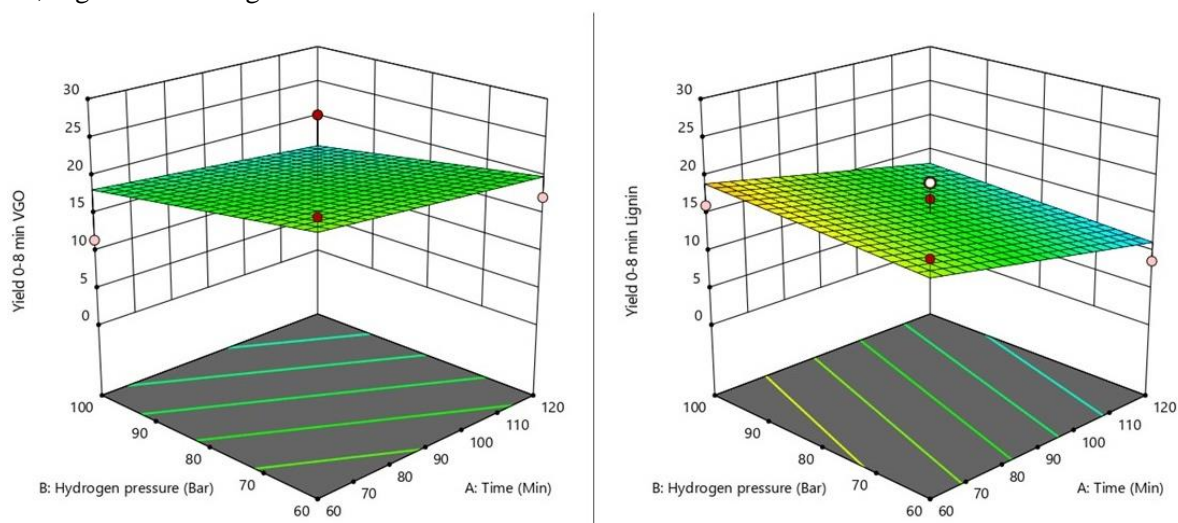


Figure 30. Central composite design results showing how the parameters of initial  $H_2$  and time affect the overall yield of relevant carbon molecules in the interval of 0-8 min. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design Expert 11 and later modified for easier comparison. Red and while dots show the data points from the experiments.

Figure 30 shows that the yield in the carbon molecules in the gasoline range is lower for the samples with lignin. The lignin samples also show a higher susceptibility to both parameters by having the yield

ranging from about 11 to 19 w%. In contrast, the yield of the VGO experiments ranged 16-22 w%. The highest yield for lignin (19 w%) is found at high H<sub>2</sub> and shorter duration. VGO best yield (22 w%) is found at low H<sub>2</sub> and shorter duration of time.

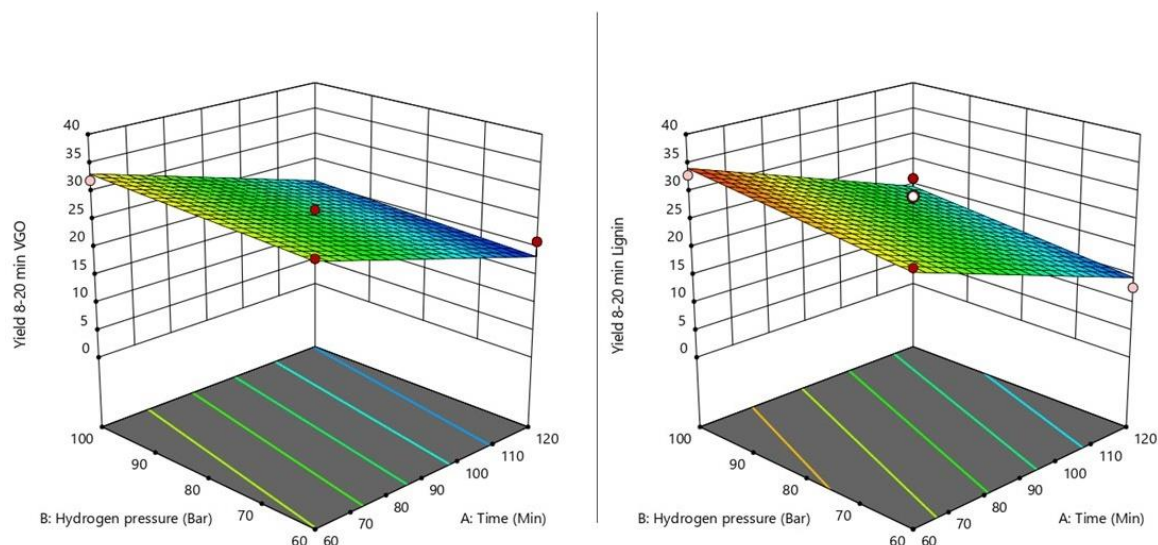


Figure 31. Central composite design results showing how the parameters of initial H<sub>2</sub> and time affect the overall yield of relevant carbon molecules in the interval of 8-20 min. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design expert 11 and later modified for easier comparison. Red and white dots show the data points from the experiments.

Figure 31 shows a similar pattern for both experiments with and without lignin regarding the effect of the parameters. The yields from the VGO experiments varies between about 18-33 w%, while yields from the lignin experiments varies between 15-34 w%. Furthermore, the yields from the lignin experiments is slightly higher at low treatment time and at high H<sub>2</sub> pressure.

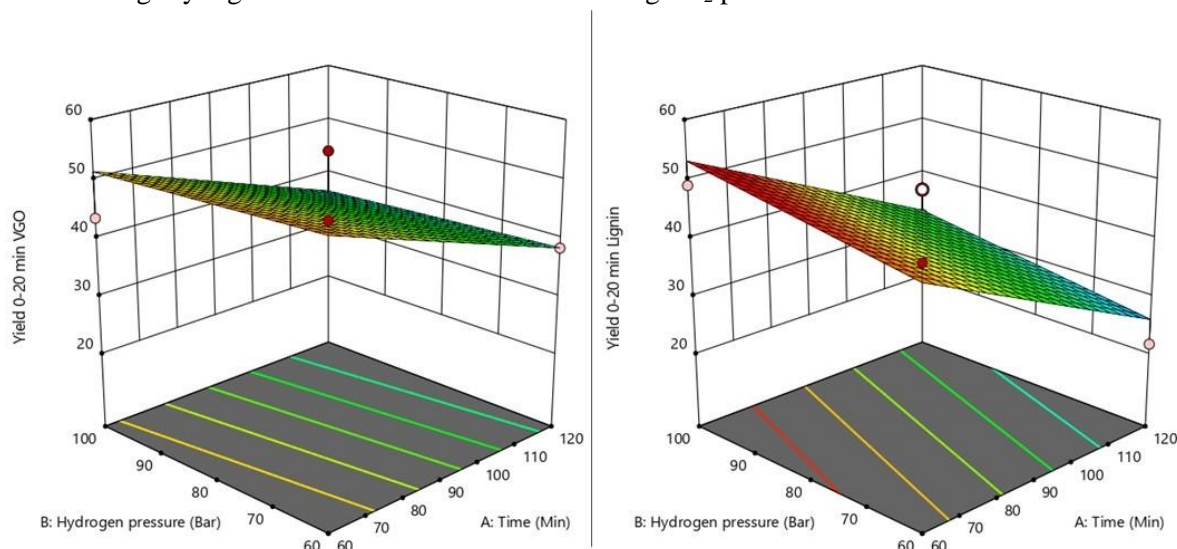


Figure 32. Central composite design results showing how the parameters of initial H<sub>2</sub> and time affect the overall yield of carbon molecules in the interval of 0-20 min. Left figure showing VGO only and right showing experiment with 10 w% lignin. Pictures generated by Design expert 11 and later modified for easier comparison. Red and white dots show the data points from the experiments.

Looking at Figure 32, the overall yield of carbon molecules in the interval of 0-20 min, varies between about 38-52 w% for the VGO experiments and about 26-52 w% for lignin experiments. The highest yields of the lignin experiments were at a high content of H<sub>2</sub> and at low treatment time, while VGO's yield peak is at both low time and H<sub>2</sub> pressure. However, noteworthy about VGO is that there is not

much effect visible regarding the H<sub>2</sub> parameter. Its effect on VGO is therefore neglectable, probably due to more than enough H<sub>2</sub> present in all experiments.

In some of the experiments, the samples were left to cool over the night or the weekend. While others were emptied hours later when the reactor was below a temperature of 30 °C, it is assumed that no further reaction happened at low temperatures. The H<sub>2</sub> consumption of MEX 1 somewhat verifies this. However, it is still another source of uncertainty.

### 4.3 Overall discussion

Looking at the results and discussion presented above, lignin is clearly much more prone to forming coke at longer durations, but also lignin seems to be much more sensitive to the amount H<sub>2</sub> than pure VGO. Furthermore, as indicated by the slope of the graphs in figure 30-32, the optimal range for lignin fuel production seems to be outside the range of the factorial design. However, overall there were limits to the method and the equipment used in these experiments, as previously mentioned and most important ones summarised below.

**Uncertainty of results.** As previously mentioned, there were large differences in the results of MEX 9, 9.1, 13 and 13.1, which were set at identical parameter settings. While it was shown that those variations were not as large as the overall difference of yields, it is non the less of major concern regarding the method and equipment used in this thesis.

**Leaks.** During the hydrotreatment experiments there were many leaks found during initiation. Although no experiments were started with obvious leaks, it is still a source of uncertainty in all the experiments. Furthermore, the results suggest that leaks either are first noticeable at high pressures and temperatures, or that they occur after an extended time due to damage to the packing.

**Long heating and cooling phases.** As seen in the in the temperature and pressure profiles above there are long heating and cooling phases during these experiments. It is in this report assumed that minimal reactions are happening at these instances. Therefore, the time of heating and cooling is not included in the time parameter set in the design of experiment. However most likely this simplification is not true, instead it is likely that there is at least some degree of HG happening. But because of how long it took to withdraw a sample given the time needed for cooling combined with the disassembling of the reactor it is not suitable to use the current equipment and method for analysing. Furthermore, the effect of coke formation by heating and cooling is difficult to determine in this study. Also, it was quite clear that the equipment could not keep up with the endothermic reactions, thus a heat exchanger with a higher output would be needed for more accurate results/analysis.

**Coke.** In these experiments there were much coke being formed. In the experiments with long reaction times and relatively low amounts of H<sub>2</sub>, the difference in coke formation between lignin and non-lignin experiments, exceeded the amount of lignin present. Thus, it is not possible in those experiments to determine if all lignin was reduced to coke and gas.

**Temperature.** Since it was not possible to keep the temperature constant during the reaction phase, the heater was not entirely appropriate for the task.

Overall, by considering the previous results as well as the limitations with the equipment and method, better yields for lignin were indicated to be towards low reaction time with higher amounts of H<sub>2</sub>.

## 5 Conclusion and future work

Regarding the work in the pre-treatment section, there were large losses of lignin in the MeOH/Acetone/water wash of the lignin during POLO. This reduced the possible amount of experiments with lignin. Furthermore, there were some metals still present in the purified lignin, and it is possible that the metal content caused interference with the activity of the catalyst.

A method and central composite design interval were decided upon by the characteristics of VGO after treatment. The selected interval and temperature were based on MEX 6 (480 °C). It is not certain whether this is the optimal temperature for lignin. It could be that the lower temperatures of MEX 1-5 would be the better alternatives, when it comes to fuel production. As indicated by the graphs of yields in figures 30-32 in the previous section. However, the semi-solid behaviour of the products in MEX 1-5 indicated low conversion. Thus, the interval of parameters similar to MEX 6 was chosen.

After analysing the results of the design of experiments, the gasoline and diesel production from both lignin and the VGO only experiments were found to be very sensitive to the reaction time. Also, the fuel production of especially lignin, was shown to be much more sensitive to the H<sub>2</sub> pressure than the VGO-only experiments. This was shown by the models used in the graphs of figures 30-32. Furthermore, the VGO-only experiments in most cases produced more diesel and gasoline than the lignin experiments. This was especially noticeable when the hydrotreatment was more severe. However, there were lignin experiments that produced more gasoline and diesel than their VGO-only counterparts did. These were found in the experiments with low treatment time, as well as with high H<sub>2</sub> pressure. Thus, the general direction for further lignin hydrotreatment research therefore seems to be towards lower treatment time and higher H<sub>2</sub> pressure.

### 5.1 Future work

The POLO version, which was used in this thesis needs to be further examined. Solubility studies on different samples of lignin with varying degrees of MeOH/water/Acetone, with the effect on solubility and metal content removal, needs to be conducted.

An interesting idea would be to optimize the yield of specific molecules. Perhaps in such a way that it would increase the yield of compounds such as benzene or toluene, which are of higher value. Perhaps an alternative could be to have a tube reactor or two sequential reactors with two sections of possibly different catalyst. Additionally, there could be an intermediate section containing either a flash or side stream withdrawal, which would subsequently be sent to the inlet main distillation tower of a petrochemical plant. This would enable a flexible system which enable a large span of customization depending on the product specification.

A wide variety of catalysts should be tested on samples of lignin from different pulp mills. The reason for this is that the wood used in different pulp mills could be of different kinds of trees. Thus, the treatment of the wood as well as the resulting lignin molecules after extraction could be different.

As stated in the theory regarding hydrocracking, the general setup is that both the feeds and the catalyst are preheated before being subjected to each other. By having a similar design, the issues of reactions occurring while heating would be greatly reduced. One possibility could be to add a mechanism which either drops or lowers the catalyst into the liquid in the reactor. Perhaps it could be possible to have a



basket like structure, which at the push of a button, opens the basket and thus drops the catalyst. Furthermore, the cooling phase could also be shortened by blowing cooled air on the reactor.

Another idea would be to build a pilot plant, where sampling is possible at various reaction temperatures and pressures. This would presumably facilitate better mapping of the actual reactions that occur during lignin's conversion to various substances. Larger volume experiments coupled with distillation could also be an alternative way to in-depth analyse the products.

The results showed that the treatment selected was too harsh, thus lower temperatures needs to be evaluated. However, it could turn out that even higher temperatures, at very short treatment times is optimal. Especially, when different lignin sources, different catalysts as well as the process economics are examined. Thus, both higher and lower temperatures need to be evaluated.

Another idea to further analyse the product as well as the reaction mechanisms, would be to analyse the gas which was formed in the experiments. Possibly in future experiments, there could be a system added which could take small gas samples at different times. Another possibility would be that the gas could be collected and examined following each experiment. For instance, the sulphur and water content in the gas, could give indications of carbon-heteroatom bonds which were cleaved during hydrotreating, as the parameters, catalysts and reactants are changed.

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## 7 Appendix

### 7.1 Raw data

The following tables contain raw and calculated data utilizing Excel and Compass as well as the result from the ICP-OES analysis.

Sample	Time (min)	H2 pressure (bar)	H2 (g)	VGO or VGO/lignin (g)	Total mass in (g)	Filtered Liquid (g)	Autoclave before (g)	Autoclave after (g)	Gas after (g)	Coke (g)
MEX 7	60.0	101.7	2.95	150.4	155.8	123.0	14260.8	14244.6	16.2	14.1
MEX 7.1	60.0	100.1	2.90	151.8	157.2	114.20	14264.8	14241.2	23.6	16.9
MEX 8	120.0	100.0	2.90	152.0	157.4	69.2	14267.6	14203.6	64.0	21.7
MEX 8.1	120.0	99.3	2.88	150.4	155.8	70.0	14266.2	14215.8	50.4	32.9
MEX 9	90.0	80.9	2.34	150.6	155.4	91.2	14267.6	14221.4	46.2	15.5
MEX 9.1	90.0	80.4	2.33	150.2	155.0	101.8	14267.6	14234.2	33.4	17.3
MEX 10	132.0	80.2	2.32	150.2	155.0	63.8	14268.0	14214.0	54.0	34.7
MEX 10.1	132.0	80.0	2.32	150.6	155.4	51.4	14271.4	14210.2	61.2	40.3
MEX 11	60.0	60.0	1.74	150.8	155.0	118.0	14270.0	14246.0	24.0	10.5
MEX 11.1	60.0	60.2	1.74	150.4	154.6	103.8	14270.0	14245.0	25.0	23.3
MEX 12	90.0	51.5	1.49	150.2	154.2	91.6	14269.6	14230.3	39.3	20.8
MEX 12.1	90.0	51.5	1.49	150.8	154.8	74.0	14273.2	14231.0	42.2	36.1
MEX 13	90.0	80.0	2.32	151.2	156.0	105.8	14269.6	14237.6	32.0	15.7
MEX 13.1	90.0	81.5	2.36	150.2	155.1	80.8	14266.0	14228.2	37.8	34.0
MEX 14	47.5	80.0	2.32	151.0	155.8	128.4	14267.6	14251.4	16.2	8.7
MEX 14.1	47.5	80.0	2.32	150.2	155.0	120.0	14267.4	14249.8	17.6	14.9
MEX 15	120.0	60.6	1.76	150.4	154.7	78.6	14267.0	14215.8	51.2	22.4
MEX 15.1	120.0	60.4	1.75	150.8	155.0	47.2	14266.6	14207.0	59.6	45.7
MEX 16	90.0	107.6	3.12	146.6	152.2	101.0	14263.8	14224.4	39.4	9.3
MEX 16.1	90.0	107.9	3.13	150.0	155.6	98.2	14265.2	14227.6	37.6	17.3

Sample	Coke (w%)	Gas after (w%)	Liquid (w%)	Area 0-8 min	Area 8-20 min	Area 0-20 min	Liq * Area 0-8 min	Liq * Area 8-20 min	Liq * Area 0-20 min
MEX 7	9.1	10.4	78.9	14.15	39.11	53.26	17.40	48.11	65.51
MEX 7.1	10.8	15.0	72.6	21.51	43.76	65.27	24.57	49.98	74.54
MEX 8	13.8	40.7	44.0	25.56	43.18	68.74	17.69	29.88	47.57
MEX 8.1	21.1	32.4	44.9	22.97	45.90	68.87	16.08	32.13	48.21
MEX 9	10.0	29.7	58.7	27.65	42.11	69.76	25.21	38.41	63.62
MEX 9.1	11.2	21.5	65.7	28.32	43.14	71.46	28.83	43.91	72.74
MEX 10	22.4	34.8	41.2	24.87	42.37	67.25	15.87	27.03	42.90
MEX 10.1	25.9	39.4	33.1	27.05	42.33	69.38	13.90	21.76	35.66
MEX 11	6.8	15.5	76.1	31.04	39.88	70.92	36.63	47.05	83.68
MEX 11.1	15.1	16.2	67.1	28.27	43.15	71.41	29.34	44.78	74.13
MEX 12	13.5	25.5	59.4	47.11	32.70	79.81	43.15	29.96	73.11
MEX 12.1	23.3	27.3	47.8	31.00	41.75	72.75	22.94	30.89	53.84
MEX 13	10.1	20.5	67.8	39.98	38.43	78.40	42.30	40.65	82.95
MEX 13.1	21.9	24.4	52.1	31.67	40.42	72.09	25.59	32.66	58.25
MEX 14	5.6	10.4	82.4	15.17	43.43	58.61	19.48	55.77	75.25
MEX 14.1	9.6	11.4	77.4	18.28	43.78	62.06	21.93	52.54	74.47
MEX 15	14.5	33.1	50.8	33.02	40.59	73.61	25.96	31.90	57.86
MEX 15.1	29.5	38.4	30.4	27.91	41.18	69.09	13.17	19.44	32.61
MEX 16	6.1	25.9	66.4	42.88	39.43	82.30	43.30	39.82	83.13
MEX 16.1	11.1	24.2	63.1	32.48	40.53	73.00	31.89	39.80	71.69

Markus labels	Al 394.40 (ppm)	As 193.69 (ppm)	Ba 233.53 (ppm)	Ca 317.93 (ppm)	Cd 214.44 (ppm)	Cr 284.33 (ppm)	Cu 327.39 (ppm)
Efter POLO	80.947	0.216	4.839	6.595	-0.016	102.296	1.264
Efter POLO	87.190	-0.746	5.192	8.991	-0.016	111.800	1.397
AVERAGE	<b>84.07</b>	<b>&lt; 0.1</b>	<b>5.02</b>	<b>7.79</b>	<b>&lt; 0.1</b>	<b>107.05</b>	<b>1.33</b>
Förtvattat	79.395	-0.857	3.588	13.161	0.079	123.367	0.771
Förtvattat	78.705	-0.389	3.483	13.439	0.085	126.181	0.841
AVERAGE	<b>79.05</b>	<b>&lt; 0.1</b>	<b>3.54</b>	<b>13.30</b>	<b>0.08</b>	<b>124.77</b>	<b>0.81</b>
Innan POLO	151.109	0.499	8.153	907.798	0.318	99.044	0.999
Innan POLO	145.043	-0.463	8.013	878.001	0.275	96.784	0.992
AVERAGE	<b>148.08</b>	<b>&lt; 0.1</b>	<b>8.08</b>	<b>892.90</b>	<b>0.30</b>	<b>97.91</b>	<b>1.00</b>
Markus labels	Fe 238.20 (ppm)	K 766.49 (ppm)	Mg 285.21 (ppm)	Mo 202.03 (ppm)	Mn 257.61 (ppm)	Na 589.59 (ppm)	Ni 231.60 (ppm)
Efter POLO	24.542	2.329	3.547	37.378	0.770	3.818	28.904
Efter POLO	28.372	2.584	6.543	40.545	0.860	5.780	30.048
AVERAGE	<b>26.46</b>	<b>2.46</b>	<b>5.05</b>	<b>38.96</b>	<b>0.82</b>	<b>4.80</b>	<b>29.48</b>
Förtvattat	44.753	15.245	7.678	27.818	4.768	55.093	23.594
Förtvattat	43.850	15.183	7.372	27.888	4.655	52.500	23.864
AVERAGE	<b>44.30</b>	<b>15.21</b>	<b>7.53</b>	<b>27.85</b>	<b>4.71</b>	<b>53.80</b>	<b>23.73</b>

Innan POLO	84.710	5522.878	333.015	23.739	171.468	37204.043	52.141
Innan POLO	83.392	5365.426	327.912	22.879	168.890	36251.299	53.174
AVERAGE	<b>84.05</b>	<b>5444.15</b>	<b>330.46</b>	<b>23.31</b>	<b>170.18</b>	<b>36727.67</b>	<b>52.66</b>
Markus labels	<b>P 213.62 (ppm)</b>	<b>Pb 220.35 (ppm)</b>	<b>Si 251.61 (ppm)</b>	<b>Sr 421.55 (ppm)</b>	<b>Ti 334.94 (ppm)</b>	<b>V 292.46 (ppm)</b>	<b>Zn 213.86 (ppm)</b>
Efter POLO	1.316	-1.135	84.601	0.089	1.691	4.783	4.328
Efter POLO	1.510	-0.947	91.501	0.103	1.870	5.165	4.706
AVERAGE	<b>1.41</b>	<b>&lt; 0.1</b>	<b>88.05</b>	<b>0.10</b>	<b>1.78</b>	<b>4.97</b>	<b>4.52</b>
Förtvattat	1.598	-0.446	284.836	0.102	1.549	4.865	17.380
Förtvattat	1.911	-0.759	281.198	0.098	1.429	4.681	17.043
AVERAGE	<b>1.75</b>	<b>&lt; 0.1</b>	<b>283.02</b>	<b>0.10</b>	<b>1.49</b>	<b>4.77</b>	<b>17.21</b>
Innan POLO	125.958	-0.325	360.096	3.088	1.197	4.466	35.910
Innan POLO	122.874	-0.619	352.450	3.011	1.117	4.665	34.858
AVERAGE	<b>124.42</b>	<b>&lt; 0.1</b>	<b>356.27</b>	<b>3.05</b>	<b>1.16</b>	<b>4.57</b>	<b>35.38</b>

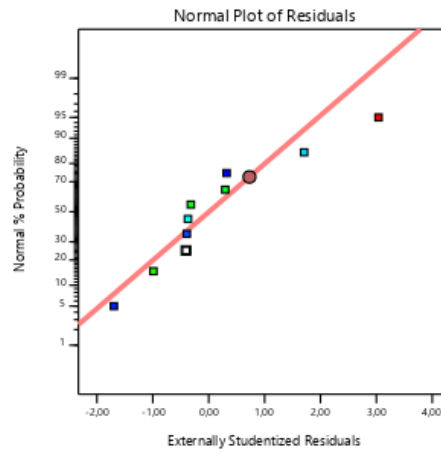
## 7.2 Regression analysis

The following regression analysis is made using Design expert 11. All the plots are related to the graphs present in the result section. Some of the following plots show a few points which exceeds the limit in Design expert 11. Perhaps those experiments should have been examined by repeating those. However due to time limitation, that is not possible. The plots and graphs presented here and in the results are selected by Design expert 11 automatic functions but also verified by manual trial and error of different models.

**Design-Expert® Software**

**Coke (VGO)**

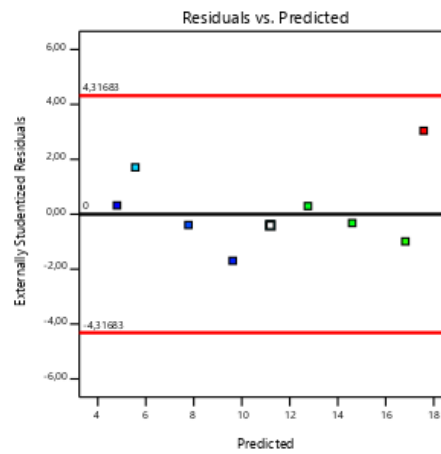
Color points by value of  
Coke (VGO):



**Design-Expert® Software**

**Coke (VGO)**

Color points by value of  
Coke (VGO):



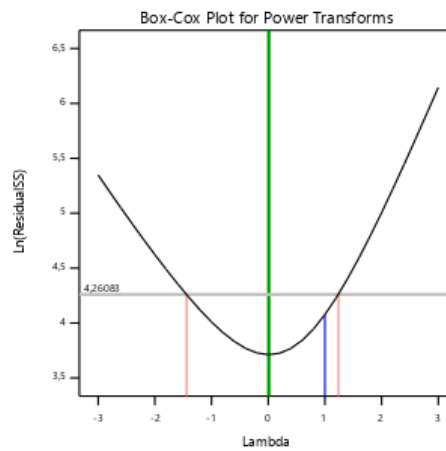
**Design-Expert® Software**

**Coke (VGO)**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,01  
CI for Lambda: (-1,44, 1,24)

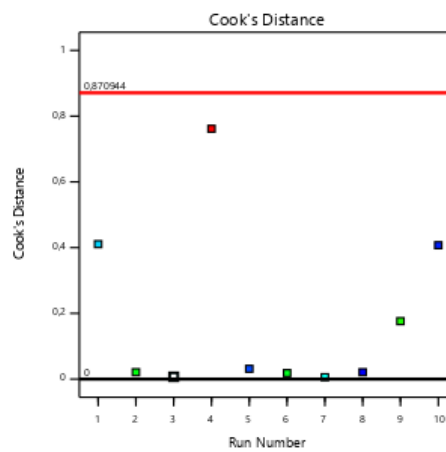
Recommended transform:  
None  
(Lambda = 1)



**Design-Expert® Software**

**Coke (VGO)**

Color points by value of  
Coke (VGO):

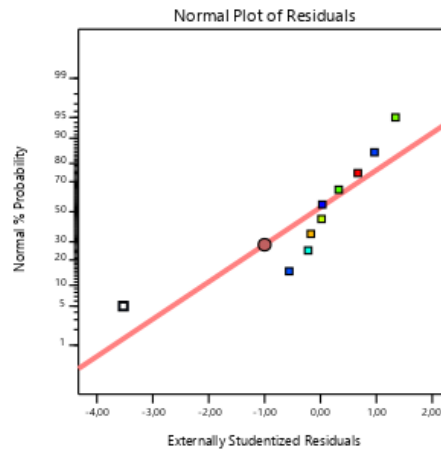


**Design-Expert® Software**

**Coke (Lignin)**

Color points by value of  
Coke (Lignin):

9,6  29,5

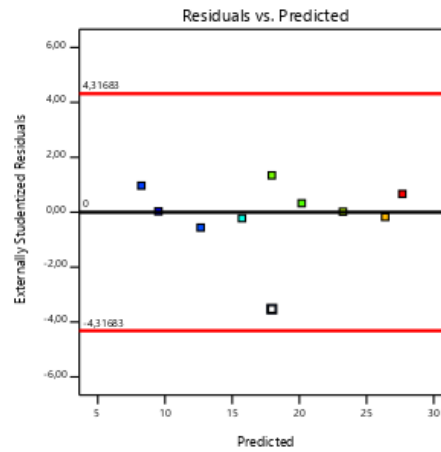


**Design-Expert® Software**

**Coke (Lignin)**

Color points by value of  
Coke (Lignin):

9,6  29,5



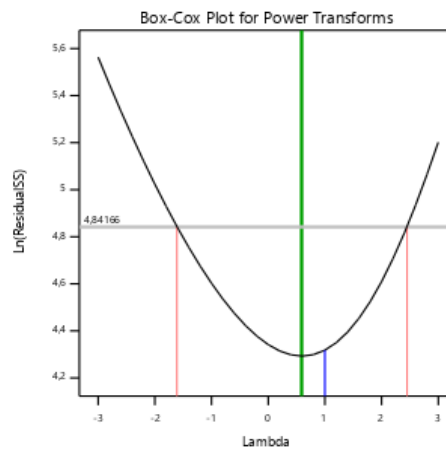
**Design-Expert® Software**

**Coke (Lignin)**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,59  
CI for Lambda: (-1,61, 2,45)

Recommended transform:  
None  
(Lambda = 1)

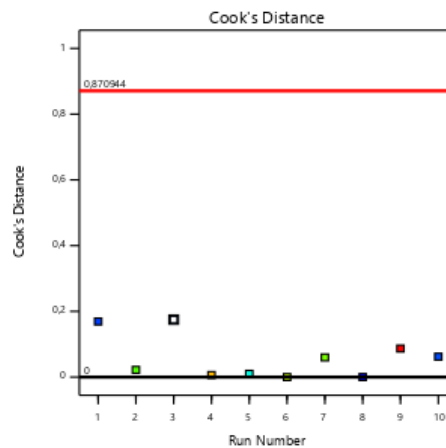


**Design-Expert® Software**

**Coke (Lignin)**

Color points by value of  
Coke (Lignin):

9,6  29,5



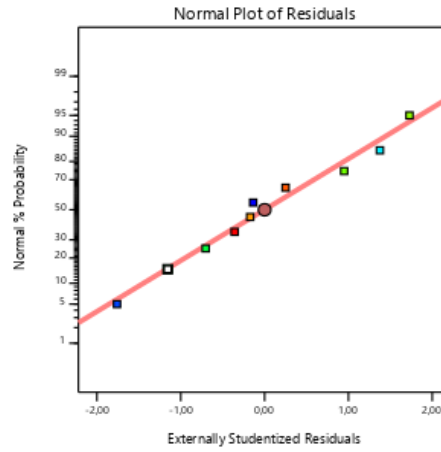


**Design-Expert® Software**

**Liquid (VGO)**

Color points by value of Liquid (VGO):

41,2  82,4

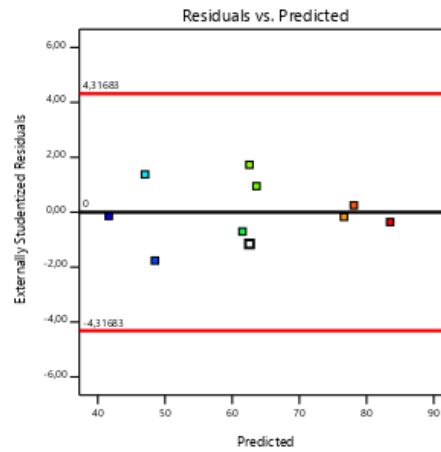


**Design-Expert® Software**

**Liquid (VGO)**

Color points by value of Liquid (VGO):

41,2  82,4



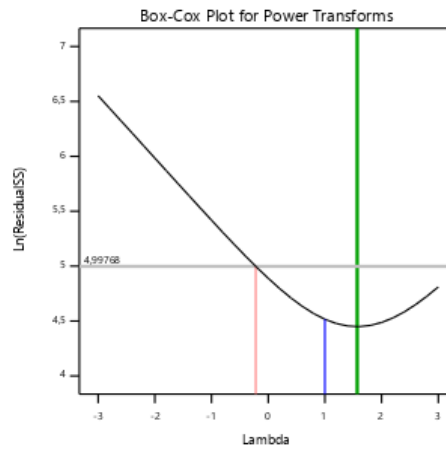
**Design-Expert® Software**

**Liquid (VGO)**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 1,57  
CI for Lambda: (-0,22, 3,39)

Recommended transform:  
None  
(Lambda = 1)

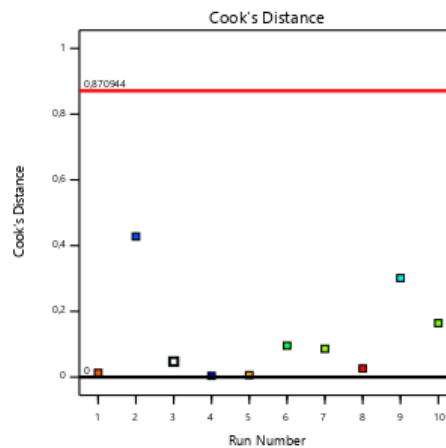


**Design-Expert® Software**

**Liquid (VGO)**

Color points by value of Liquid (VGO):

41,2  82,4

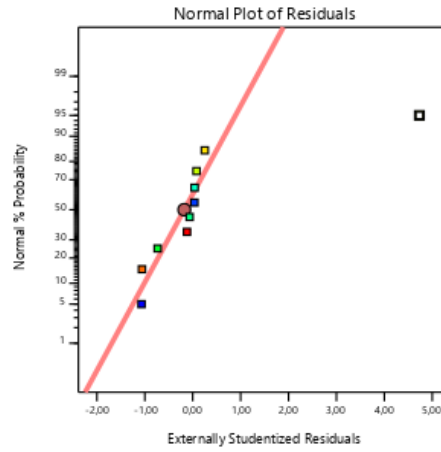


**Design-Expert® Software**

**Liquid (Lignin)**

Color points by value of Liquid (Lignin):

30,4  77,4

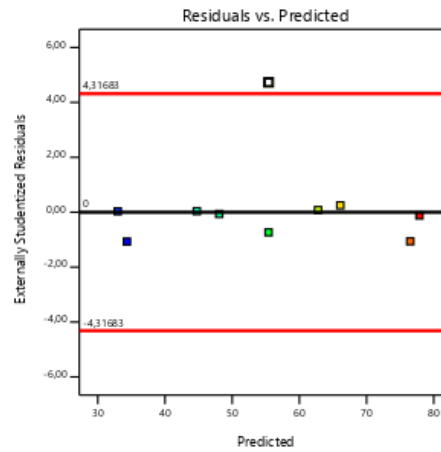


**Design-Expert® Software**

**Liquid (Lignin)**

Color points by value of Liquid (Lignin):

30,4  77,4



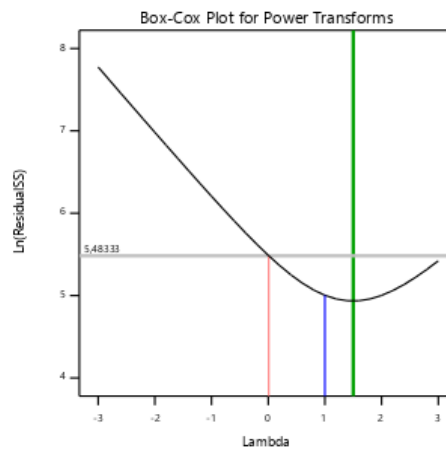
**Design-Expert® Software**

**Liquid (Lignin)**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 1,5  
CI for Lambda: (0,01, 3,11)

Recommended transform:  
None  
(Lambda = 1)

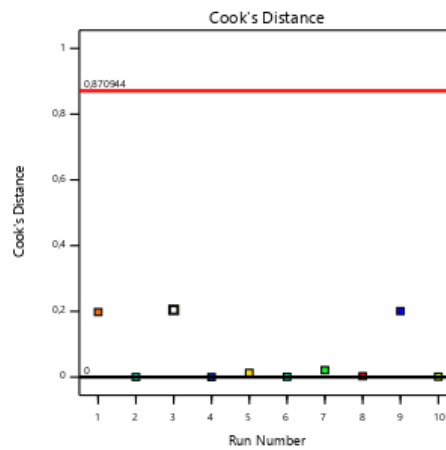


**Design-Expert® Software**

**Liquid (Lignin)**

Color points by value of Liquid (Lignin):

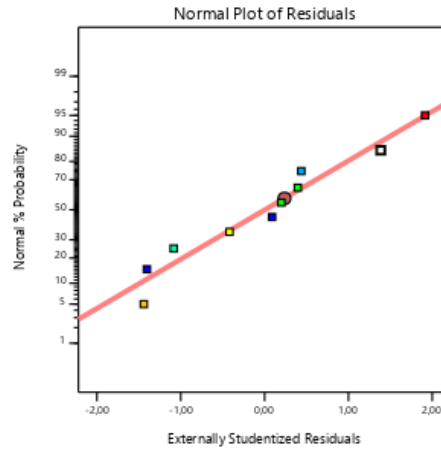
30,4  77,4



**Design-Expert® Software**

**Gas (VGO)**

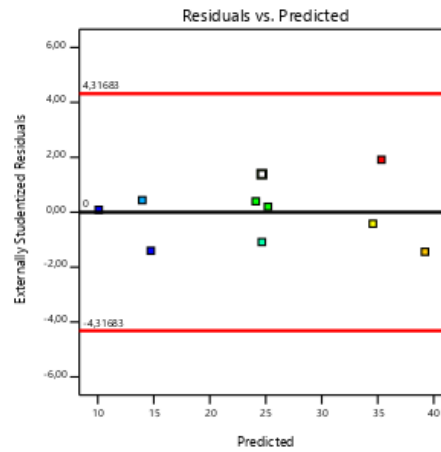
Color points by value of Gas (VGO):



**Design-Expert® Software**

**Gas (VGO)**

Color points by value of Gas (VGO):



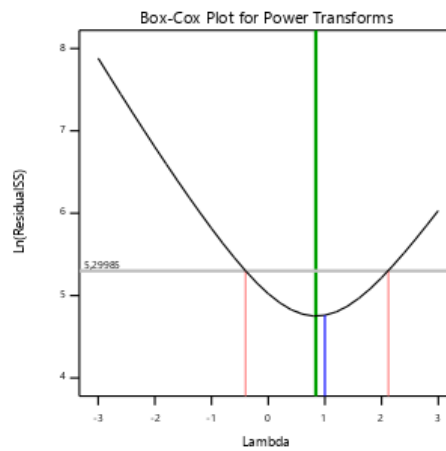
**Design-Expert® Software**

**Gas (VGO)**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,84  
CI for Lambda: (-0,4, 2,12)

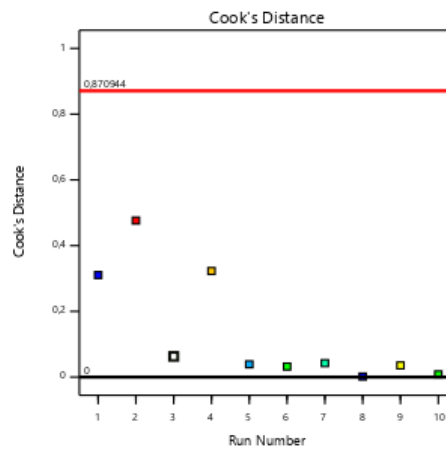
Recommended transform:  
None  
(Lambda = 1)



**Design-Expert® Software**

**Gas (VGO)**

Color points by value of Gas (VGO):



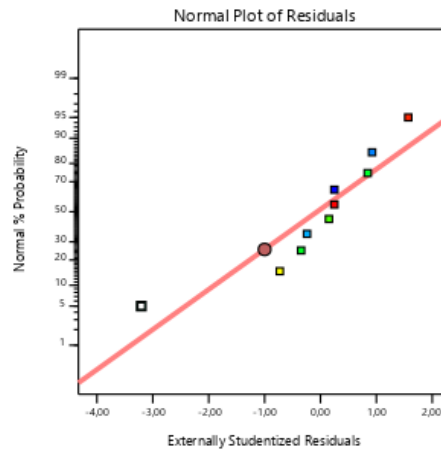
**Design-Expert® Software**

**Gas (Lignin)**

Color points by value of

Gas (Lignin):

11,4  39,4



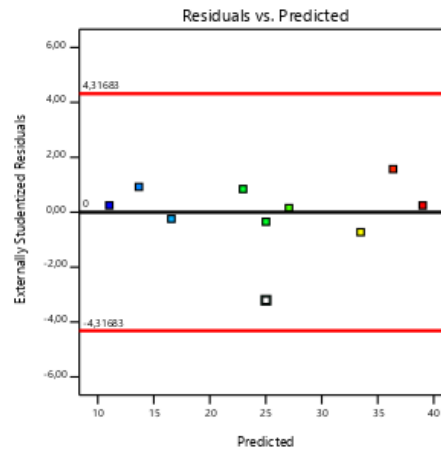
**Design-Expert® Software**

**Gas (Lignin)**

Color points by value of

Gas (Lignin):

11,4  39,4



**Design-Expert® Software**

**Gas (Lignin)**

Current transform:

None

Current Lambda = 1

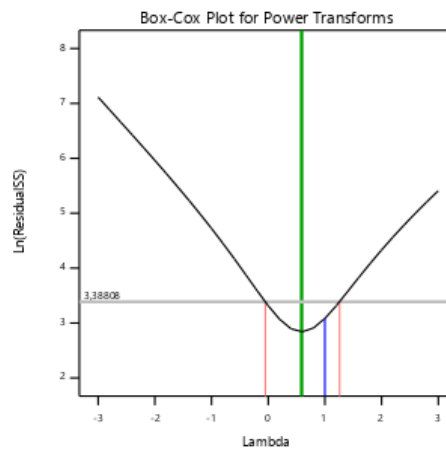
Best Lambda = 0,59

CI for Lambda: (-0,05, 1,26)

Recommended transform:

None

(Lambda = 1)

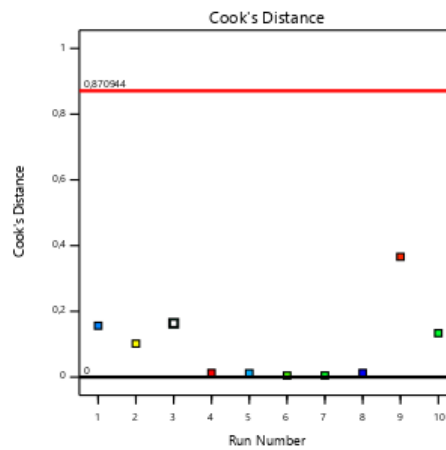


**Design-Expert® Software**

**Gas (Lignin)**

Color points by value of  
Gas (Lignin):

11,4  39,4

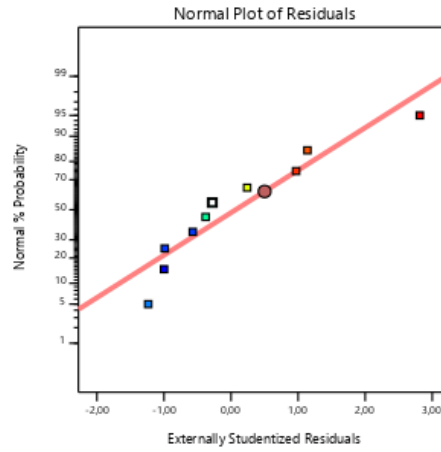


**Design-Expert® Software**

**Yield 0-8 min VGO**

Color points by value of Yield 0-8 min VGO:

10,57  29,54

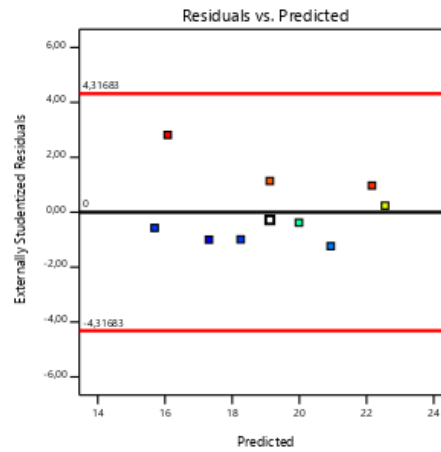


**Design-Expert® Software**

**Yield 0-8 min VGO**

Color points by value of Yield 0-8 min VGO:

10,57  29,54



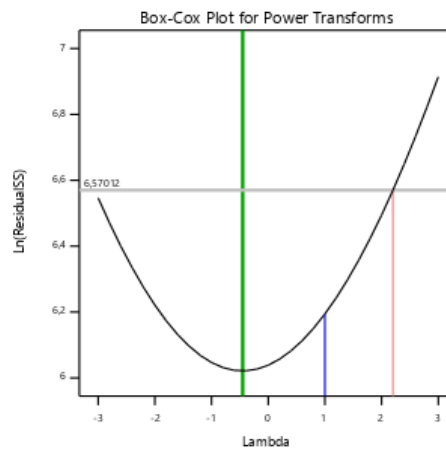
**Design-Expert® Software**

**Yield 0-8 min VGO**

Current transform:  
None

Current Lambda = 1  
Best Lambda = -0,45  
CI for Lambda: (-3,06, 2,2)


Recommended transform:  
None  
(Lambda = 1)

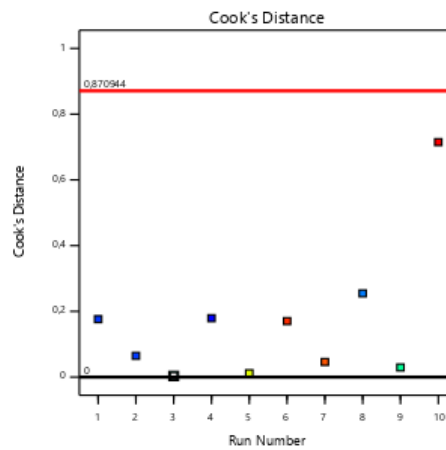


**Design-Expert® Software**

**Yield 0-8 min VGO**

Color points by value of Yield 0-8 min VGO:

10,57  29,54

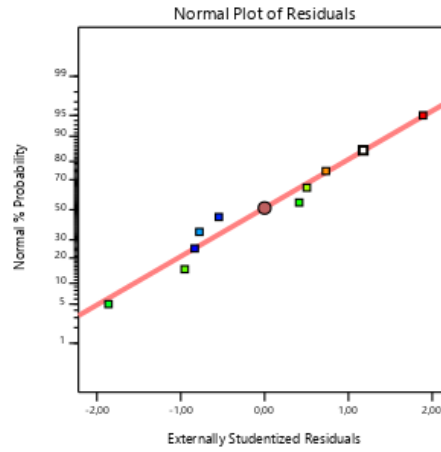


**Design-Expert® Software**

**Yield 0-8 min Lignin**

Color points by value of Yield 0-8 min Lignin:

8,74  21,26

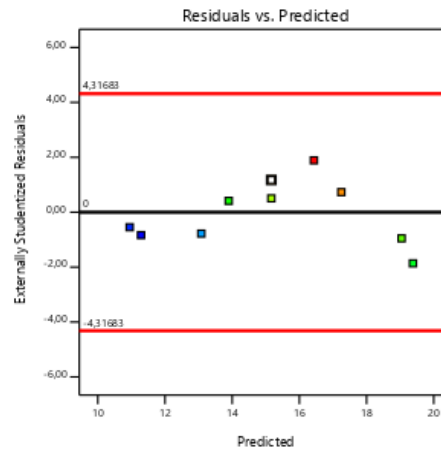


**Design-Expert® Software**

**Yield 0-8 min Lignin**

Color points by value of Yield 0-8 min Lignin:

8,74  21,26



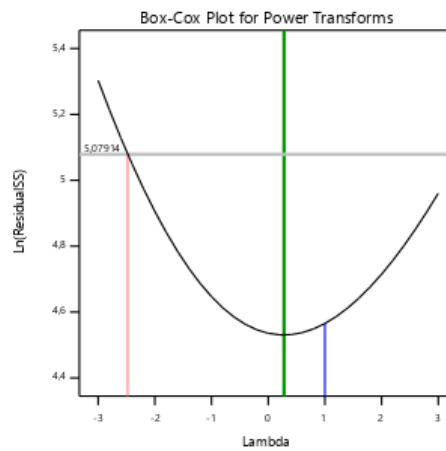
**Design-Expert® Software**

**Yield 0-8 min Lignin**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,28  
CI for Lambda: (-2,48, 3,39)


Recommended transform:  
None  
(Lambda = 1)

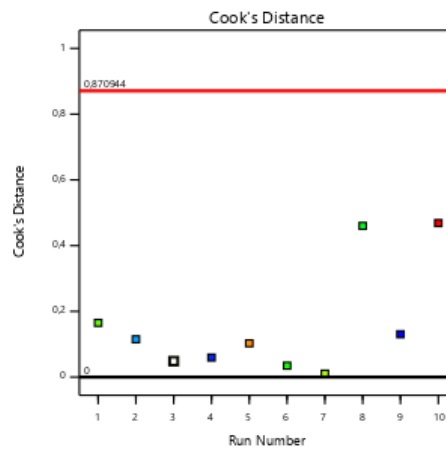


**Design-Expert® Software**

**Yield 0-8 min Lignin**

Color points by value of Yield 0-8 min Lignin:

8,74  21,26

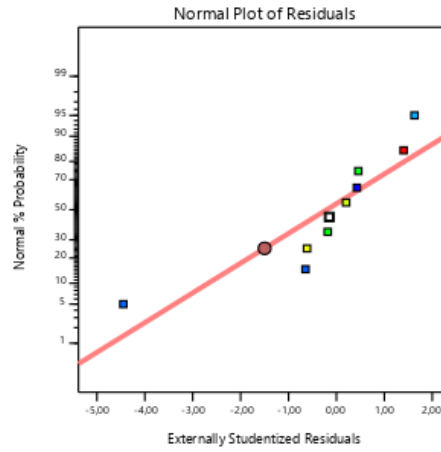


**Design-Expert® Software**

**Yield 8-20 min VGO**

Color points by value of Yield 8-20 min VGO:

18  36,93

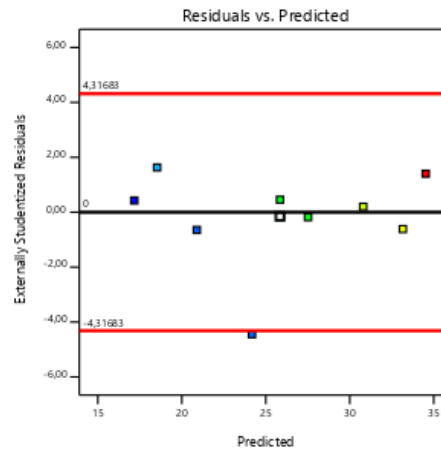


**Design-Expert® Software**

**Yield 8-20 min VGO**

Color points by value of Yield 8-20 min VGO:

18  36,93



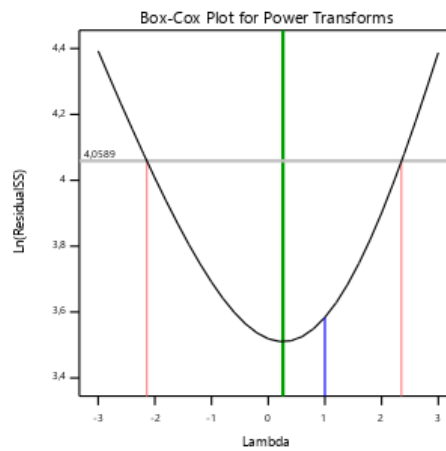
**Design-Expert® Software**

**Yield 8-20 min VGO**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,26  
CI for Lambda: (-2,14, 2,35)

Recommended transform:  
None  
(Lambda = 1)

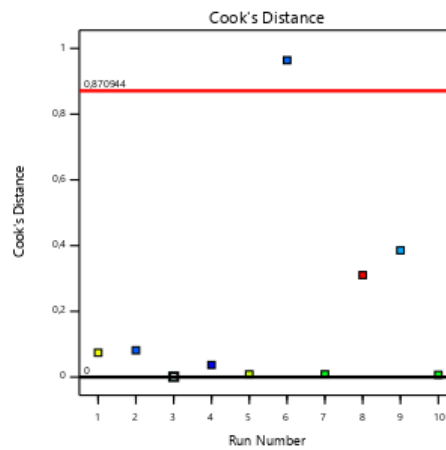


**Design-Expert® Software**

**Yield 8-20 min VGO**

Color points by value of Yield 8-20 min VGO:

18  36,93

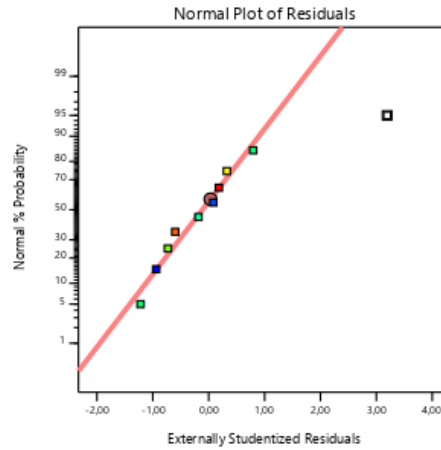


**Design-Expert® Software**

**Yield 8-20 min Lignin**

Color points by value of Yield 8-20 min Lignin:

12,89  34,98

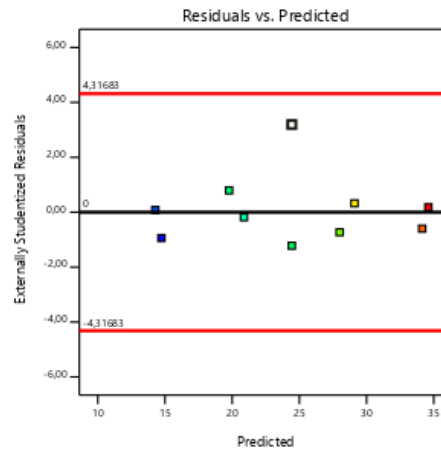


**Design-Expert® Software**

**Yield 8-20 min Lignin**

Color points by value of Yield 8-20 min Lignin:

12,89  34,98



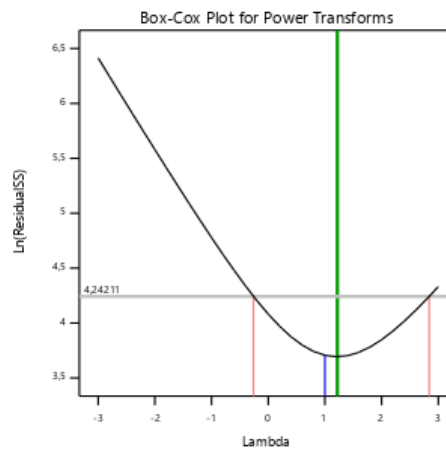
**Design-Expert® Software**

**Yield 8-20 min Lignin**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 1,22  
CI for Lambda: (-0,26, 2,84)

Recommended transform:  
None  
(Lambda = 1)

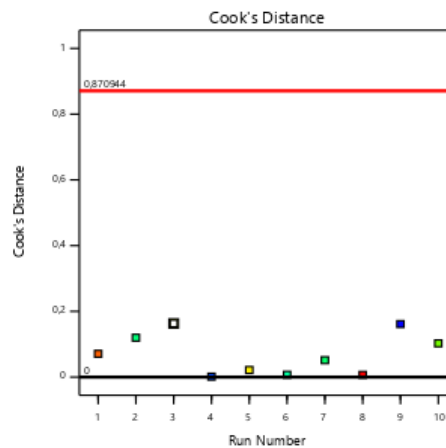


**Design-Expert® Software**

**Yield 8-20 min Lignin**

Color points by value of Yield 8-20 min Lignin:

12,89  34,98



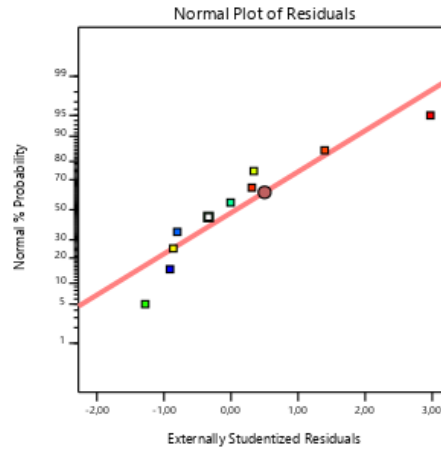


**Design-Expert® Software**

**Yield 0-20 min VGO**

Color points by value of Yield 0-20 min VGO:

28,56  56,7

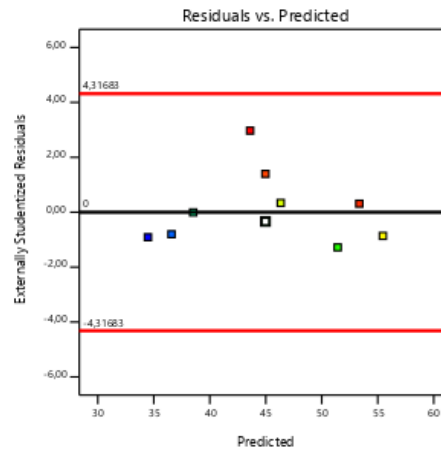


**Design-Expert® Software**

**Yield 0-20 min VGO**

Color points by value of Yield 0-20 min VGO:

28,56  56,7



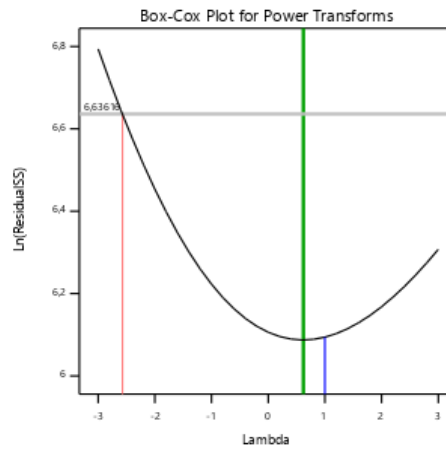
**Design-Expert® Software**

**Yield 0-20 min VGO**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,62  
CI for Lambda: (-2,57, 4,59)

Recommended transform:  
None  
(Lambda = 1)

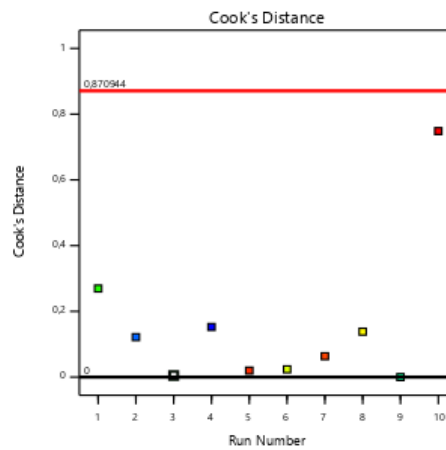


**Design-Expert® Software**

**Yield 0-20 min VGO**

Color points by value of Yield 0-20 min VGO:

28,56  56,7

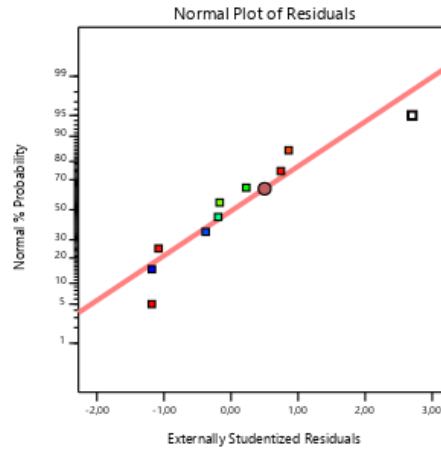


**Design-Expert® Software**

**Yield 0-20 min Lignin**

Color points by value of Yield 0-20 min Lignin:

21,62  49,58

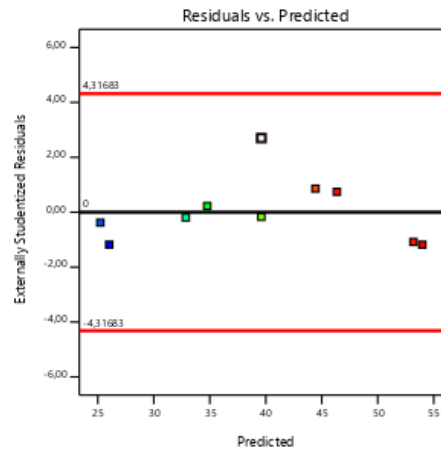


**Design-Expert® Software**

**Yield 0-20 min Lignin**

Color points by value of Yield 0-20 min Lignin:

21,62  49,58



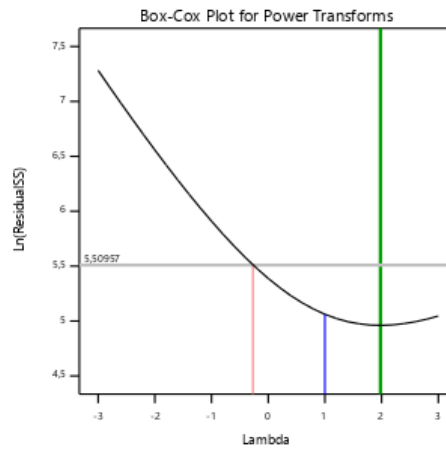
**Design-Expert® Software**

**Yield 0-20 min Lignin**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 1,98  
CI for Lambda: (-0,27, 4,76)

Recommended transform:  
None  
(Lambda = 1)

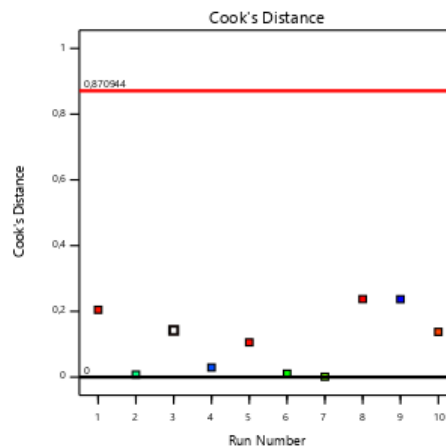


**Design-Expert® Software**

**Yield 0-20 min Lignin**

Color points by value of Yield 0-20 min Lignin:

21,62  49,58

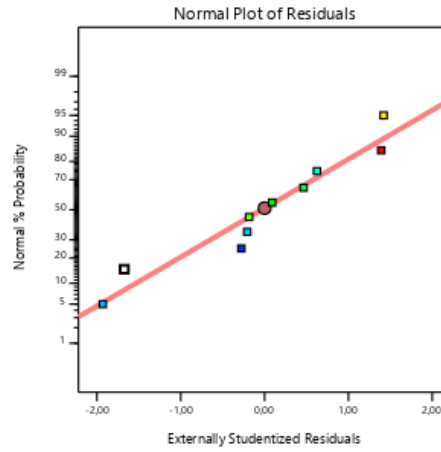


**Design-Expert® Software**

**w% coke difference**

Color points by value of w% coke difference:

1,19  15,51

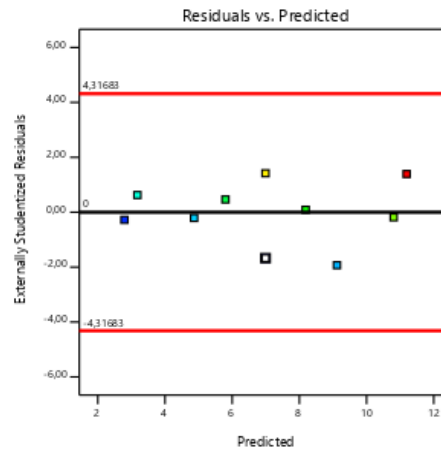


**Design-Expert® Software**

**w% coke difference**

Color points by value of w% coke difference:

1,19  15,51



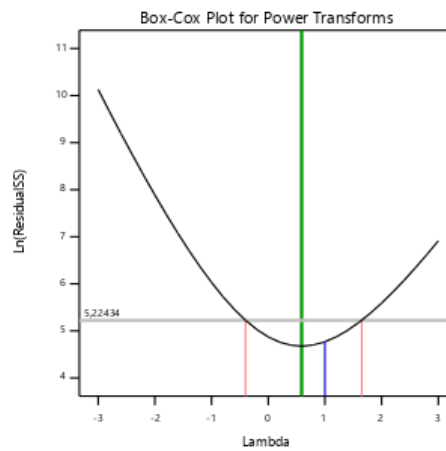
**Design-Expert® Software**

**w% coke difference**

Current transform:  
None

Current Lambda = 1  
Best Lambda = 0,59  
CI for Lambda: (-0,4, 1,65)


Recommended transform:  
None  
(Lambda = 1)



**Design-Expert® Software**

**w% coke difference**

Color points by value of w% coke difference:

1,19  15,51

