

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**HYDRODEOXYGENATION OF LIGNIN MODEL COMPOUNDS TO
LIQUID FUEL COMPONENTS**

M.Sc. THESIS

Osman KURŞUN

Department of Chemical Engineering

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AUGUST 2012

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(506101022)

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Thesis Advisor: Prof. Dr. Serdar YAMAN

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**LİGNİN MODEL BİLEŞİKLERİNİN SIVI YAKIT BİLEŞENLERİNE
HİDRODEOKSİJENASYONU**

YÜKSEK LİSANS TEZİ

**Osman KURŞUN
(506101022)**

Kimya Mühendisliği Anabilim Dalı

Kimya Mühendisliği Programı

Tez Danışmanı: Prof. Dr. Serdar YAMAN

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Osman KURŞUN
Chemical Engineer

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ABBREVIATIONS

FT	: Fischer-Tropsch
DCM	: Dichloromethane
BCD	: Base Catalysed Depolymerization
BPE	: Benzyl phenyl ether
HTWL	: High Temperature Liquid Water
T_g	: Glass Transition Temperature
TGA	: Thermogravimetric Analysis
FTIR	: Fourier Transform Infrared Spectrometry
GG	: Guaiacylglycerol- β -guaiacyl ether
GC/MS	: Gas Chromatography-Mass Spectroscopy
GC/FID	: Gas Chromatography-Flame Ionization Detector
TEM	: Transmission electron microscopy

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HYDRODEOXYGENATION OF LIGNIN MODEL COMPOUNDS TO LIQUID FUEL COMPONENTS

SUMMARY

Use of biomass as a resource for energy production is increasingly a focus in both research and development projects, and producing renewable liquid fuels that are suitable for use in motor vehicles is one of the greatest challenges in the biofuel area.

Sustainable utilization of biomass must include using all three components of the raw material, not just the most easily convertible fractions, such as cellulose and hemicellulose. Although lignin is one of the most abundant parts of lignocellulosic biomass, it usually remains as a waste. However, considering its chemical structure, it can be a good resource for production of aromatic units.

There are different types of linkages found in lignin, and phenolic units are connected to each other via these linkages. Linkages found in lignin are mostly represented by lignin model compounds that are proper reactants to better understand the principle chemistry and conversion pathways.

Recently, direct one-step conversion of lignin into liquid fuels has gained considerable interest. Even though there are alternative pathways for this purpose, it seems that hydrodeoxygenation is one of the most promising processes to obtain liquid fuels with increased energy density in the presence of H₂.

In this study, monomeric and dimeric lignin model compounds were performed in the presence of Pt/C catalyst under conditions of 200 °C and 20 bar H₂. As to phenol hydrodeoxygenation; reaction time, reaction medium acidity, and catalyst particle size effect were investigated. Regarding dimeric model compounds such as diphenyl ether, benzyl phenyl ether, biphenyl, and diphenyl methane, reaction time and reaction medium acidity effect were inquired.

According to experimental findings, it was found that reactant conversion was positively affected by increasing the reaction time in all cases. In phenol experiments, cyclohexanol, cyclohexanone and cyclohexane were detected as the main products, but the selectivities were depending on the reaction medium and catalyst used.

Aside from Pt/C, it was seen that Ru/C and Ru/Al₂O₃ also showed a catalytic activity for phenol conversion. Besides, experimental findings showed that increasing the mean Pt particle size from 2.03 nm to 3.09 nm caused in a decrease for phenol conversion.

On the other hand, under applied conditions for dimeric model compounds, it was observed that C-C bond cleavage could not be accomplished while C-O bond cleavage was easily achieved, and this led to monomeric product generation especially when diphenyl ether and benzyl phenyl ether were the reactants.

Moreover, full hydrogenation of aromatic ring was observed for all reactants. Also, the reaction medium acidity affected the product distribution significantly when the reactants were diphenyl ether and benzyl phenyl ether. Yet, as the bond cleavage was not observed for diphenyl methane and biphenyl, therefore acidity of reaction medium did not cause in a change for overall conversion and product distribution of these compounds.

LİGNİN MODEL BİLEŞİKLERİNİN SIVI YAKIT BİLEŞENLERİNE HİDRODEOKSİJENASYONU

ÖZET

Dünya üzerinde gün geçtikçe artan insan nüfusu ve sanayileşme, enerjiye olan talebi de hızlı bir şekilde artırmıştır. Mevcut olan enerji kaynakları arasında fosil yakıtlar, gerek çevreye olan olumsuz etkileri gerekse rezervlerinin sınırlı olmasından dolayı araştırmacıları yenilenebilir, temiz ve verimli alternatifler bulmaya yöneltmiştir.

Günümüzde fosil yakıtlara alternatif olabilecek çeşitli yenilenebilir enerji kaynakları bulunmakla beraber, biyokütle enerjisi bu kaynaklar içerisinde en gelecek vaat edenidir. Bir çok yenilenebilir enerji kaynağı çoğunlukla doğrudan elektrik üretmek için kullanılırken, biyokütlenin kimyasal yapısı sıvı yakıt eldesine de imkan verdiğinden, onu diğer kaynaklar arasında daha da önemli kılar. Özellikle biyokütlenin motorlu taşıtlara uygun sıvı formda bir yakıtla dönüştürülmesi, biyoyakıt alanında çalışılan en önemli konulardan bir tanesidir.

Biyokütlenin biyoetanol üretimi için önemli bir girdi olduğu günümüzde, ikinci nesil biyoetanol rafinerileri lignoselülozik biyokütle kullanımına yönelerek, biyokütlenin yalnızca kolay dönüştürülebilir kısımları olan selüloz ve hemiselülozdan değil de, bunların yanında lignin kısmından da yararlanmayı amaçlamaktadır.

Her ne kadar lignin biyokütlenin en verimli bileşenlerinden bir tanesi de olsa, mevcut olan biyorafineriler içerisinde birinci nesil olarak tarif edilen biyorafineriler, biyokütlenin lignin kısmını atık olarak bırakmaktaydı ve atık yan ürün olarak elde edilen bu lignin, genellikle proseslerde ısı elde etmek amacıyla yakılmaktaydı. Fakat ligninin sahip olduğu kimyasal yapı düşünüldüğünde, onun aromatik yapıda bileşenler üretimine iyi bir kaynak olabileceği görülmektedir.

Ligninin kimyasal yapısında, aromatik bileşenleri bir arada tutan farklı türde bağlar bulunmaktadır. Ligninin yapısında bulunan bu bağlar, genellikle lignin model bileşikleriyle temsil edilirler. Ligninin fenolik ürünlere dönüşüm mekanizması, bu dönüşümün dayandığı temel kimyasal reaksiyonların belirlenmesi ve bağların uygulanan fiziksel ve kimyasal şartlar altında nasıl davrandığının incelenmesi, genellikle model bileşiklerin kullanılmasıyla gerçekleştirilir.

Biyokütlenin temel bileşenlerinden olan ligninden enerji yoğunluğu yüksek yeni ürünler elde etmek amacıyla çeşitli dönüşüm yöntemleri geliştirilmiştir. Günümüz şartlarında lignine uygulanan dönüşüm yöntemleri içerisinde gazlaştırma ve piroliz yoğun bir şekilde incelenmektedir.

Gazlaştırma prosesinde ligninden elde edilen sentez gazının Fischer-Tropsch yöntemiyle sıvı formda yakıtlara dönüştürülmesi mümkün olabilse de, bu proseste

kullanılan katalizörlerin pahalı olması ve Fischer-Tropsch sentezinde hidrojen için ara dengeleme operasyonu gerekmesi uygulamayı zorlaştırmaktadır.

Diğer taraftan lignine, biyokütlede olduğu gibi doğrudan piroliz işlemi de uygulanabilir. Fakat, ligninin pirolizi sonrasında elde edilen sıvı ürün yüksek miktarda oksijen içerdiğinden, büyük oranda su ve suda çözünebilir bileşenler ihtiva ettiğinden ve bu sıvı genellikle asidik karakterde olduğundan, iyi bir sıvı yakıt özelliği kazanabilmesi için ikinci bir iyileştirme prosesine tabi tutulmalıdır.

Ligninden doğrudan sıvı yakıt elde etmeye yönelik olarak geliştirilen diğer bir yöntem ise hidrodeoksijenasyondur. Bu yöntemde lignin fenolik bileşenlere parçalanır ve uygun katalizör varlığında fenolik bileşenlerin oksijen içeriği azaltılırken hidrojen içeriği artılır.

Bu çalışmada, monomerik ve dimerik çeşitli lignin model bileşiklerinin hidrodeoksijenasyonu 200 °C ve 20 bar H₂ varlığında gerçekleştirilmiştir. Monomerik model bileşik olarak sadece fenol incelenirken, dimerik model bileşik olarak ise diphenyl ether, benzyl phenyl ether, diphenyl methane ve biphenyl incelenmiştir.

Fenolün reaktant olduğu çalışmalarda; reaksiyon süresi, reaksiyon ortamının asiditesi, kullanılan ticari Pt/C katalizörünün parçacık boyutu ve ticari Ru/C, Ru/Alumina katalizörlerinin reaksiyon sonu ürünlerine ve fenol dönüşümüne olan etkileri araştırılmıştır. Dimerik model bileşiklerinin reaktant olduğu çalışmalarda ise, reaksiyon süresi ve reaksiyon ortamının asiditesinin reaksiyon sonu ürünlerine ve reaktant dönüşümüne olan etkileri sadece Pt/C katalizör varlığında incelenmiştir.

DeneySEL bulgular göstermektedir ki, reaksiyon süresinin artması bütün reaktantların son ürünlere dönüşümünü pozitif yönde etkilemiştir. Fenolün reaktant olduğu çalışmalarda, Pt/C, Ru/C ve Ru/Alumina katalizörlerinin fenol dönüşümünü yüksek oranda desteklediği görülmüştür. Pt/C katalizör varlığında gerçekleştirilen çalışmalarda fenol ortalama 1 saat içerisinde tamamen tükenmiştir. Ru/C'nun katalizör olarak kullanıldığı çalışmalarda ise fenolün ortalama 2 saat içerisinde tamamen son ürünlere dönüştüğü görülmüştür. Ru/Alumina katalizör varlığında, 4 saat sonundaki fenol dönüşümü % 88 olarak hesaplanmıştır.

Normal reaksiyon ortamında fenolden elde edilen en baskın son ürün cyclohexanol olurken, cyclohexanone genellikle ara ürün olarak elde edilmiştir. Reaksiyon ortamına fosforik asitin eklendiği çalışmalar göstermektedir ki, reaksiyon ürünleri dağılımı reaksiyon ortamının asit ihtiva etmesinden önemli ölçüde etkilenmektedir. Fosforik asitin kullanıldığı çalışmalarda cyclohexanol ara ürün olarak bulunurken, cyclohexane dominant ürün olarak elde edilmiştir.

Normal reaksiyon ortamında Pt/C katalizör varlığında gerçekleştirilen çalışmalarda eser miktarda cyclohexene ve cyclohexane da gözlemlenmiştir. Bu komponentlerin doğrudan doğruya cyclohexanone'dan oluştuğu sonucuna varılmıştır.

Pt/C katalizörün parçacık boyutunun incelendiği çalışmalar göstermiştir ki, ticari partikül boyutu 2.03 nm olan Pt/C katalizörün partikül boyutunu 3.09 ve 3.69 nm'ye artırmak fenol dönüşümünde % 20'lik bir katalitik aktivite kaybına yol açmıştır.

Ru/C ve Ru/Alumina katalizörlerinin kullanıldığı çalışmalarda az miktarda benzen oluşumu gözlemlenmiştir. Benzenin fenolden doğrudan hydrogenolysis reaksiyonu sonucu oluştuğu sonucuna varılmıştır. Ayrıca, Ru/Alumina katalizör varlığında reaksiyon son ürünleri içerisinde cyclohexanone konsantrasyonu durağan olarak gözlemlenmiştir. Bu durağanlığın alumina supportun varlığından kaynaklandığı sonucuna varılmıştır.

Dimerik model komponentlerin reaktant olduğu çalışmalar göstermektedir ki, reaksiyon sonu ürünlerinin dağılımı reaktantın kimyasal yapısına doğrudan doğruya bağlıdır. Uygulanan şartlar altında diphenyl ether ve benzyl phenyl ether'in sahip olduğu C-O bağının kırılarak monomerik yeni ürünler oluşumuna sebebiyet verdiği gözlemlenmiştir. Fakat, diphenyl methane ve biphenyl reaktant olduğu çalışmalar da bu reaktantların sahip olduğu C-C bağının kırılmadığı, dolayısıyla monomerik reaksiyon ürünlerinden ziyade bu bileşiklerden hidrojene olmuş yeni ürünler meydana geldiği görülmüştür.

Diphenyl ether'in reaktant olduğu çalışmalar göstermektedir ki, monomerik üniteler arasındaki C-O bağı homolitik bir şekilde kırılıp phenoxy ve phenyl radikallerinin oluşumuna sebebiyet vermiştir. Pt/C katalizör ve 20 bar hidrojen varlığında bu radikallerden önce benzen ve fenol oluşmuş, daha sonra bu monomerlerin de hidrojenasyonu ile benzenden cyclohexane, fenolden ise cyclohexanol oluşumu gerçekleşmiştir. Bağ kırılması ve reaktant hidrojenasyonu aynı anda başladığından, reaksiyon sonu ürünleri içerisinde bicyclohexyl de elde edilmiştir. Reaksiyon ortamının asitlendirilmesi ürün dağılımını belirgin bir şekilde etkilemiştir. Asidik durumda cyclohexanol tamamen tükenip cyclohexane'in baskın ürün olarak oluştuğu görülmüştür.

Benzyl phenyl ether'in reaktant olduğu çalışmalar göstermektedir ki, C-O bağ kırılması homolitik ve heterolitik olmak üzere iki farklı şekilde gerçekleşmiştir. Homolitik bağ kırılması sonrası oluşan fenoksi ve benzil radikalleri 20 bar hidrojen varlığında ilk önce fenol ve toluene dönüşmüş, daha sonra ise Pt/C katalizörün de varlığıyla cyclohexanol ve methylcyclohexane'a hidrojene olmuşlardır. Heterolitik bağ kırılması sonunda benzyl phenyl ether'den benzil alkol ve fenol elde edilmiş, hidrojen ve hidrojenasyon katalizör varlığında ise bu bileşenlerin cyclohexanemethanol ve cyclohexanol'e hidrojene olduğu görülmüştür. Aromatik halka hidrojenasyonu ve bağ kırılması aynı anda vukuu bulduğundan, benzyl phenyl ether'in yarı doymuş ve tam doymuş dimerleri de reaksiyon sonu ürünleri içerisinde tesbit edilmiştir. Ayrıca, reaksiyon ortamının asitlendirilmesi reaksiyon ürünleri dağılımında bir değişime sebep olmuş ve cyclohexanol'un tamamen tükenip yerine cyclohexane'in oluştuğu gözlemlenmiştir.

Diphenyl methane ve biphenyl'in reaktant olduğu çalışmalar göstermektedir ki, uygulanan şartlar altında bu reaktantların sahip olduğu C-C bağı kırılmamıştır. Fakat, ürün olarak bu reaktantların hidrojene olmuş halleri reaksiyon sonu ürünleri içerisinde tesbit edilmiştir. Reaksiyon ortamının asitlendirilmesi, reaksiyon sonu ürünleri dağılımında bir değişikliğe yol açmadığı gibi, reaktant dönüşümünde de belirleyici bir rol oynamamıştır.

1. INTRODUCTION

1.1 Background

In today's world, energy can be described as a vital input for social and economic development. In addition, energy plays one of the most important roles to ease the human life, and let the people to live in welfare. On the other hand, it is known that the population is getting higher, and the industrialization has been increased during the last century. Therefore, energy demand has enhanced all around the world, and the growth in energy use has led the researchers to find alternative energy sources.

Energy sources can be mainly classified into two groups which are nonrenewable and renewable sources. Nonrenewable energy sources cover fossil fuels such as coal, petroleum and natural gas. It is obvious that once a deposit of these fuels is depleted it cannot be replenished, and a replacement deposit must be found instead. Nonetheless, renewable energy sources are the energy sources that are continually replenished; including hydraulic, solar, wind, geothermal, wave, tidal and biomass energies.

The stocks of fossil fuels have been increasingly depleted in the last century, and due to the growing concern over the excessive emission of greenhouse gases, researchers have been forced to investigate renewable, abundant and comparably cleaner alternatives to liquid fuels and chemicals produced from petroleum [1]. Herein, chemical structure of biomass makes it more important among the renewable energy sources as it enables to obtain liquid fuel and valuable chemicals from biomass, whereas the rest of the renewable energy sources are mostly used for electricity production.

Production of ethanol from biomass, primarily starch and sugar rich components, is a well-known process. However, second-generation bioethanol processes focus on lignocellulosic biomass as a feedstock since it is relatively cheap and more abundant [2]. The concept of biorefinery is to utilize all three components of biomass efficiently. However, most of the existing biorefinery schemes have been focused on

utilizing easily convertible fractions of biomass such as cellulose and hemicelluloses, while lignin part remains as waste [3]. Besides, it is also known that paper and pulp industries produce large quantities of lignin as a byproduct, but it is mostly used for power generation in the process by burning [4]. Nevertheless, the chemical structure of lignin shows that it can be a good resource to produce valuable chemicals and liquid fuel if the chemical structure of lignin could be cleaved into smaller molecular units [5].

So far several studies have been done to convert lignin to liquid fuel additives and commercially important chemicals. For instance, H₂ and CO (syngas) can be produced from lignin by gasification process, subsequently methanol and various other chemicals can be synthesized through known technologies by using syngas. However, the gasification of biomass and subsequent application of Fischer-Tropsch (FT) catalysis is not cost effective and competitive at the moment, and also Fischer-Tropsch processes require intermediate adjustment of the hydrogen balance to produce final products [6]. Alternatively, it is possible to obtain pyrolysis oil from lignin in the way similar to biomass pyrolysis as well. Yet, pyrolysis oil produced from lignin pyrolysis contains a high level of oxygen, and includes water and water-soluble components. Also, it is not miscible with petroleum-based liquids. Moreover, this bio-oil is very acidic, corrosive and unstable for storage, thus requires further processing [3].

On the other hand, direct one-step conversion of lignin into liquid fuel or valuable chemicals has received considerable attention as a trendy pathway. The primary goal of this method is to depolymerize lignin, and deoxygenate these depolymerized compounds. By this way, aromatic hydrocarbons can be obtained with decreased oxygen content, and this will lead to increase in energy density.

1.2 Objective

Recently, studies on one-step alternatives for lignin conversion into low-oxygen content liquid fuel and monomeric phenols have been presented [5, 7, 8]. It is observed that product yield and variety of product distribution are affected by experimental conditions.

In this project, we worked on aqueous phase hydrodeoxygenation of dimeric and monomeric lignin model compounds which are benzyl phenyl ether, diphenyl ether, diphenyl methane, biphenyl and phenol. The main objective of this thesis is to produce aromatic fuel components from lignin model compounds by using Pt/C noble metal catalyst in the presence of H₂. In order to achieve this goal, bench scale experiments and characterization of liquid product by using analytical techniques were performed. It is possible to obtain optimum process conditions with having knowledge about the effect of the operating parameters on the final product. In this study, the effect of the operating parameters such as reaction time, reaction medium acidity, and catalyst particle size on the composition of liquid product were investigated. Schematic representation of research activities is given in Figure 1.1.

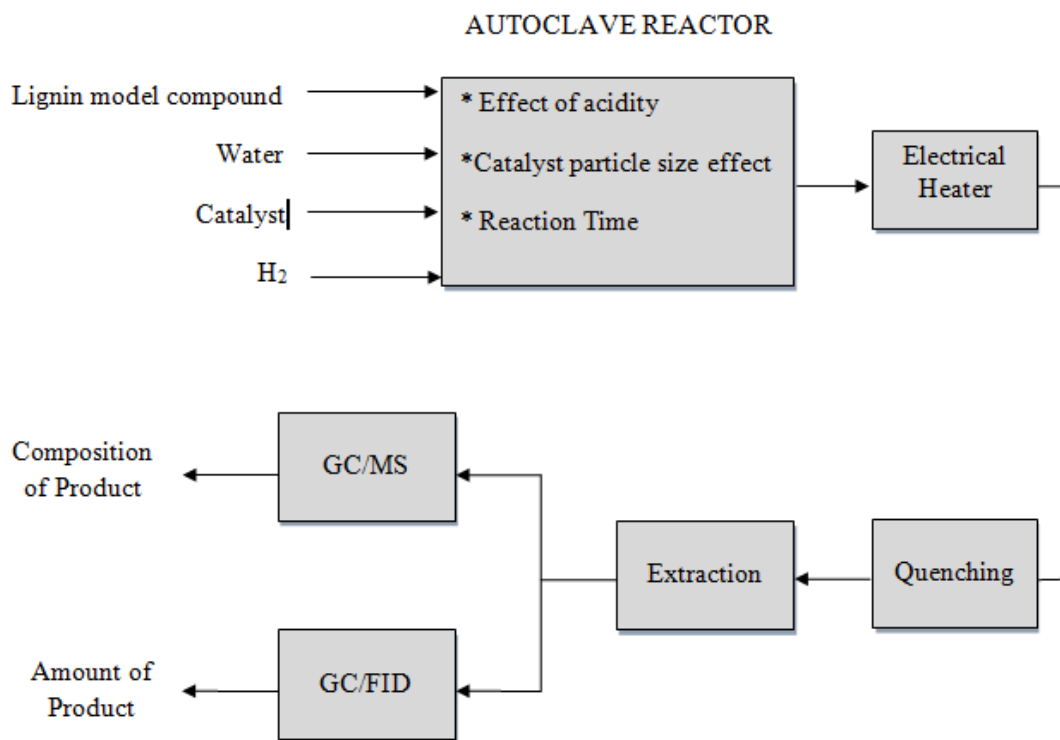


Figure 1.1 : Schematic representation of research activities.

2. BIOMASS

The term "biomass" refers to organic matter that has stored energy through the process of photosynthesis in biomass materials such as forestry residues, wood, wood waste (sawdust and wood fiber-based sludge from pulp/paper mill) and agricultural residues (wheat/rice straws and corn waste) [7]. Besides, biomass is also defined by researchers in a more legalistic way, and this definition describes biomass as “all nonfossil organic materials that have an intrinsic chemical energy content. This includes all water- and land-based vegetation and trees, or virgin biomass, and organic components of waste materials such as municipal solid waste (MSW), municipal biosolids (sewage) and animal wastes (manures), forestry and agricultural residues, and certain types of industrial wastes” [9].

We can consider feedstocks derived from biomass in three general classes which are proper for the production of renewable fuels [8]: starchy feedstocks (including sugars), triglyceride feedstocks, and lignocellulosic feedstocks. In Figure 2.1, representative chemical structures for starches and triglycerides compared to cellulose are shown.

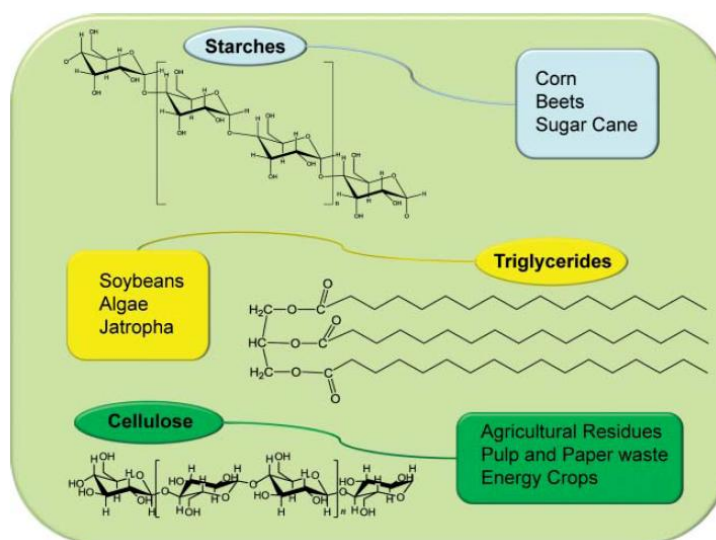


Figure 2.1 : Chemical structure of biomass feedstocks [8].

Starchy feedstocks derived from biomass are those comprised of glucose polysaccharides joined by α -glycosidic linkages, such as amylose and amylopectin. These linkages can be easily hydrolyzed into the constituent sugar monomers, therefore starchy feedstocks have been heavily used in the first generation of bioethanol process [8].

Triglyceride feedstocks consist of fatty acids and glycerol derived from both plant and animal sources. Hence, various vegetable oils, waste oil products, and algal sources which include triglycerides are used as feedstocks for the production of biodiesel [8].

Lignocellulosic biomass is the most abundant biomass type existing in the world, and it can be easily found in many crops while starch and triglycerides cannot be present in everywhere. Moreover, it is widely known that the most of the energy crops and waste biomass considered for energy production are lignocellulosic feedstocks [8].

As previously mentioned, lignocellulosic biomass is known as an abundant and inexpensive feedstock for biorefineries. As the name implies, lignocellulosic biomass consists of three basic components: cellulose, hemicelluloses, and lignin [1, 5, 8].

2.1 Cellulose

Cellulose is described as a linear polymer of glucose consisting of parts with crystalline structure and parts with amorphous structure which affect its reactivity. It accounts for 40-50 % of whole biomass depending on the plant source as well [8]. Also, it is typically isolated within the lignin/hemicelluloses matrix, and in untreated biomass, accordingly direct hydrolysis of cellulose is very difficult due to its complex distribution in biomass [8]. Figure 2.2 shows the representative structure of cellulose found in lignocellulosic biomass.

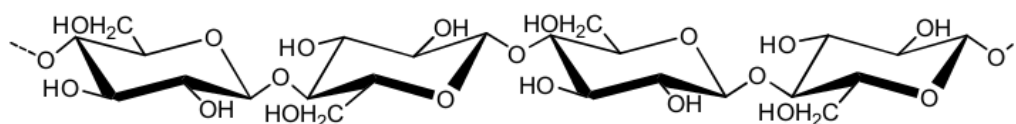


Figure 2.2 : Chemical structure of cellulose.

2.2 Hemicellulose

Hemicellulose is defined as an amorphous, heterogeneously branched polymer of pentoses and hexoses, mainly xylose, arabinose, mannose, galactose, and glucose which are linked together in different proportions depending on the type of plant [5]. Hemicellulose is bound to lignin, and cellulose strands are interlaced with hemicelluloses [8]. On the other hand, hemicellulose is the most reactive fraction among the three lignocellulosic components found in biomass, and it can account for up to 35 % of the dry biomass. The main hemicellulose groups from softwood are the arabinoglucuronoxylans, while galactoglucomannans are the majority of those found in softwoods [1]. In Figure 2.3, hemicellulose structure found in softwood is illustrated.

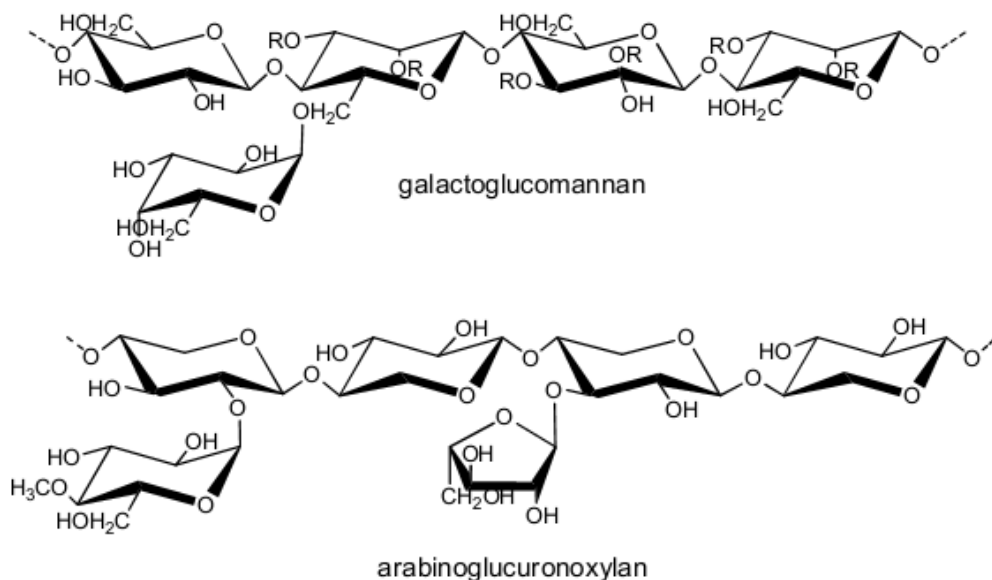


Figure 2.3 : Chemical structure of hemicellulose.

2.3 Lignin

2.3.1 Structure

The term “lignin” was used firstly by the Swiss botanist A. P. Candolle (1778-1841), from the Latin word lignum which means “wood”. Lignin forms part of the secondary cell walls of plants and helps maintain the integrity of the cellulose/hemicelluloses/pectin matrix [10]. It is one of the major components of

biomass that corresponds to 15-30 % of woody biomass, and a potential source for aromatic chemicals [11, 12].

On the other side, lignin is a natural polymer of three different phenyl-propanol units, the so-called monolignols, such as p-coumaryl alcohol, syringyl alcohol, and coniferyl alcohol [10]. These monolignols are illustrated in Figure 2.4.

On the other side, lignin is a natural polymer of three different phenyl-propanol units, the so-called monolignols, such as p-coumaryl alcohol, syringyl alcohol, and coniferyl alcohol [10]. These monolignols are illustrated in Figure 2.4.

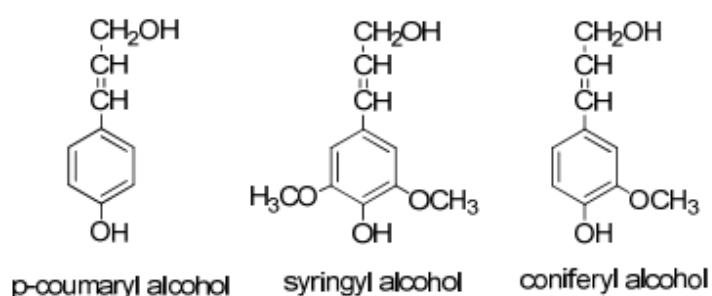


Figure 2.4 : Lignin monomeric units [10].

At present, however, there is still no consensus as to what the actual structure of lignin is, but studies on various lignin extracts have shown that the chemical structure and functional groups in lignin extracts depend significantly on the method of isolation [10]. A representative structural model of lignin proposed by Adler in 1977 is presented in Figure 2.5.

It is known that classification of lignin is based on plant taxonomy; hence type of the phenyl-propanol units found in lignin may vary. For instance, softwood lignin presents more coniferyl residues. However, hardwood lignin contains a mixture of coniferyl alcohol and syringyl alcohol, and grass lignin bears a mixture of all these three monolignols [10].

2.3.2 Linkages found in lignin

It is clear that the composition and amount of lignin varies from species to species and tree to tree. Lignin mainly consists of a variety of linkages which are irregularly connecting various aryl ethers [5]. Even though the proportion of these linkages depends on wood type, typically more than two-thirds of the linkages in lignin are ether linkages. Hardwood lignin contains about 1.5 times more β -O-4-linkages than

softwood lignin [5]. Other major linkages include β -5-, 5-5-, 4-O-5-, β -1-, α -O-4- and β - β - linkages. However, the proportion of these linkages varies considerably, and values of the linkages have been presented in Table 2.1 [5]. The functional groups of major influence on the reactivity of lignin consist of methoxyl, phenolic and aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether and carbonyl groups.

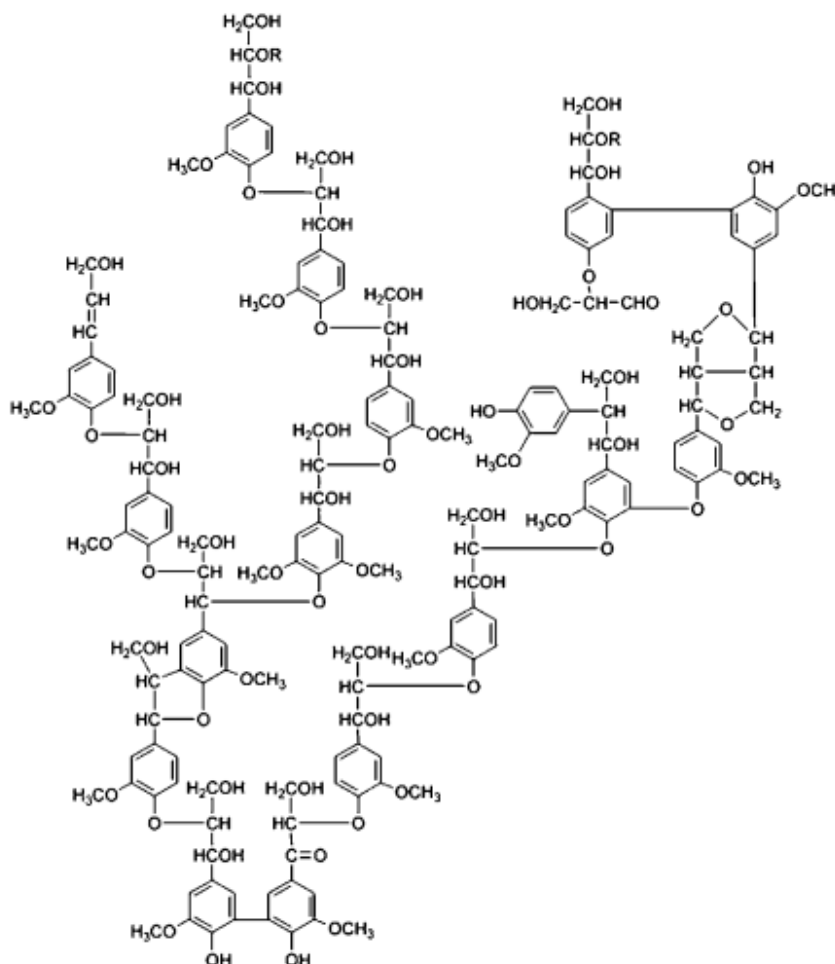


Figure 2.5 : Proposed structure of lignin by Adler [10].

Table 2.1 : Proportion of major linkages found in lignin [5].

Linkage Type	Softwood (spruce) [%]	Hardwood (birch) [%]
β -O-4-Aryl ether	46	60
α -O-4-Aryl ether	6-8	6-8
4-O-5-Diaryl ether	3.5-4	6.5
β -5-Phenylcoumaran	9-12	6
5-5-Biphenyl	9.5-11	4.5
β -1-(1,2-Diarylpropane)	7	7
β - β -(Resinol)	2	3
Others	13	5

As it is seen from Figure 2.6 that ether linkages at the α - and β - positions are the most abundant functional groups on the propanoid side chain of lignin. Under appropriate conditions, these bonds can be cleaved into smaller molecules, more particularly in phenolic units [13]. However, it is indicated that C-C bonds are more stable and stronger than C-O bonds among the units in lignin structure [5]. This chemical structure of lignin makes it important as well as other parts of biomass such as cellulose and hemicellulose.

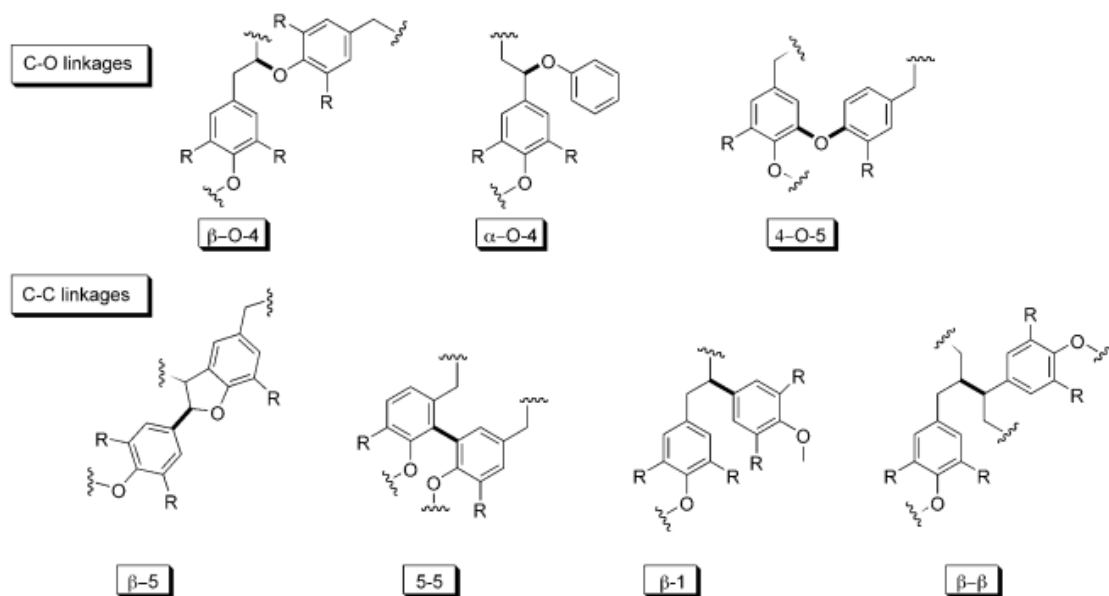


Figure 2.6 : Major linkages found in lignin [10].

2.3.3 Properties of Lignin

2.3.3.1 Molecular weight and polydispersity

In fact, the right molecular weight of lignin in wood is not known since it is not possible to isolate lignin from wood without degradation. However, it is known that different methods for measuring the molecular weight of isolated lignin give various results, and aggregation of lignin molecules may prevent determination of real molecular weight. Vapor phase pressure osmometry and light scattering are the traditional methods of analysis. According to the results obtained by using these methods, molecular weight of lignin is estimated to be 20,000 g/mol for softwood lignin, yet hardwood lignin has lower values [9].

2.3.3.2 Solution properties

It is indicated that lignin behaves as an insoluble, three dimensional network. Isolated lignins (milled wood, kraft, or organosolv lignins) show maximum solubility in solvents having a Hildebrand's solubility parameter, δ , of 20.5-22.5 (J/cm³)^{1/2} (10-11(cal/cm³)^{1/2}), and $\Delta\mu$ in excess of 0.14 μ , where $\Delta\mu$ is the ir shift in the O-D bond when the solvents are mixed with CH₃OD. Solvents meeting these requirements include dioxane, acetone, methyl cellosolve, pyridine, and dimethyl sulfoxide [9].

2.3.3.3 Thermal properties

As it is known that lignin is an amorphous polymer, therefore it shows thermoplastic character undergoing a glass-transition at temperatures that vary widely depending on the method of isolation, sorbed water, and heat treatment. Considering its fuel characteristic, it stores more energy than cellulose (qv) in wood. To illustrate, the glass transition temperature, T_g , and heat capacity at 350 K for dioxane lignin are 440 K and 1.342 J/ (g K), respectively [9].

2.3.4 Lignin model compounds

Lignin decomposition and conversion to liquid fuel and chemicals are often simplified by performing model compounds rather than lignin itself. Studies with lignin model compounds are significant in order to better understand the conversion mechanism and kinetics. Also, lignin model compounds allow us to determine the stability of intermediate products occurred during the conversion of actual lignin. Monomeric, dimeric and trimeric model compounds have been considered for studies simulating any of the three major characterizing parameters in lignin: interunit links, methoxyphenol groups, and propanoid chains [5]. Chemical structure of some well-known lignin model compounds such as benzylphenylether, diphenylether, diphenylmethane, biphenyl and phenol are illustrated in Figure 2.7.

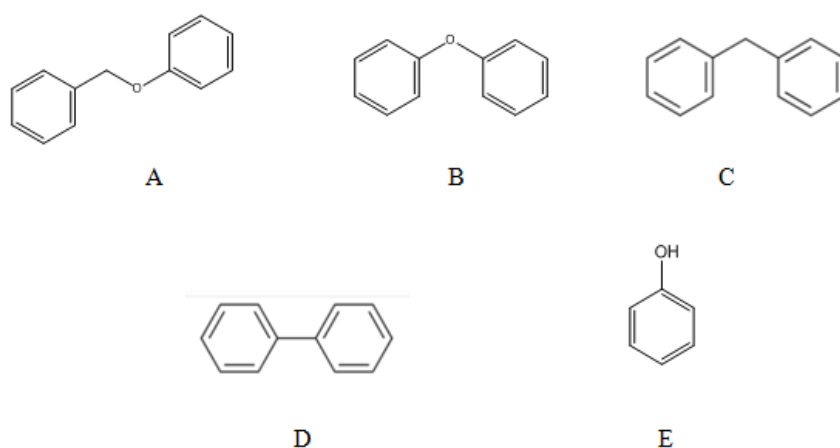


Figure 2.7 : Chemical structure of lignin model compounds: (A) benzyl phenyl ether, (B) diphenyl ether, (C) diphenyl methane, (D) biphenyl, (E) phenol.

2.3.5 Van krevelen diagram

The chemical structure of lignin is the most similar to petroleum among the different constituents of biomass. Through the action of heat and pressure over millions of years, decayed remains of ancient plants and/or animals were buried by sediments to form fossil fuels. As to their susceptibility of microbial degradation, typically it is the lignin constituent that gets left behind as ancient lignocellulosic remains [14]. In the presence of these harsh conditions, lignocellulosic remains become chemically transformed into those are being mined from the earth at this moment. Considering the coal ranks exist, the lowest form of coal is even called as lignite, which is soft, and has a brown color.

It is clear that there is no any possibility to apply tremendous geologic temperature and pressure to biomass which have been currently targeted for alternative fuels. Consequently, the challenge lies in developing new processes such as thermal, chemical/catalytic or enzymatic that can convert them into molecules which have similar chemical and physical properties as crude oil. In this respect, in the Van Krevelen diagram, the significant criteria which need to be mentioned are summarized in Figure 2.8. It is related to hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios of fossil fuels and different biomass-derived materials.

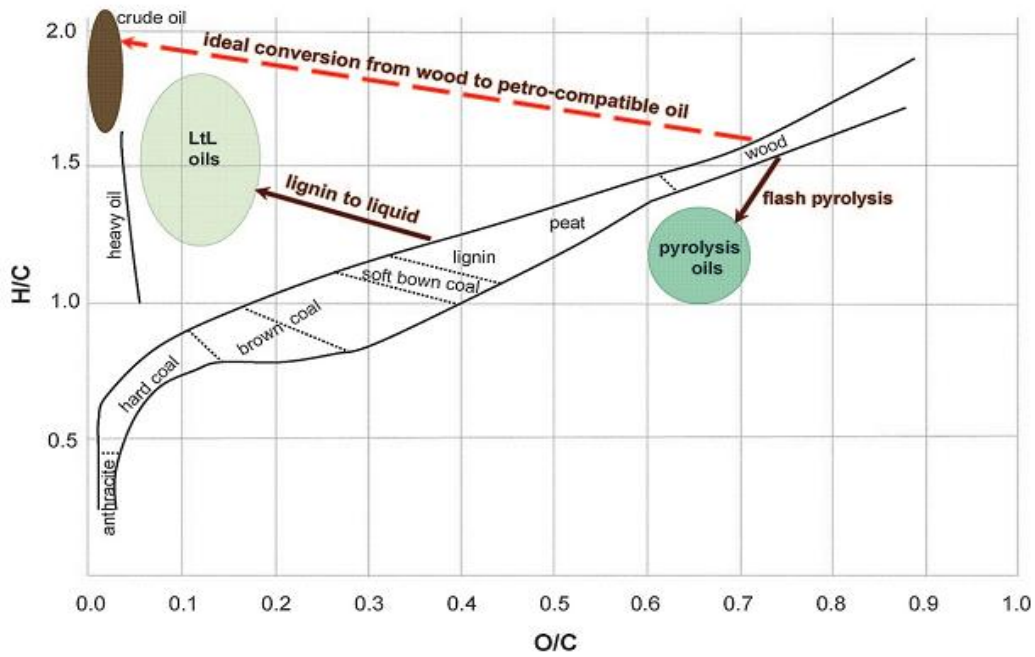


Figure 2.8 : Van Krevelen diagram showing the H/C and O/C ratios of different biomass and fossil materials [3].

In this diagram, hydrocarbons which possess only hydrogen and carbon in an H/C ratio of around 2.0 are located at the top left corner, as shown Figure 2.8. These hydrocarbons could be set as the targeted structure for lignin conversion to obtain liquid fuels. Technical lignin contains substantial amounts of oxygen, the O/C ratio ranging between 0.3 and 0.85. Due to high oxygen content and the high content of aromatic rings, the H/C ratio in technical lignin is around 0.8 to 1.3. In order to convert this lignin into the liquid fuel, oxygen content of the molecules must be eliminated, and at the same time hydrogen needs to be introduced [15].

3. LIGNIN CONVERSION

Utilization of lignin content of biomass would require some form of depolymerization or disintegration to be able to reach smaller compounds which can then be treated to produce chemicals compatible with existing petroleum based-fuels and chemicals. In this sense, considering the degradation and conversion of lignin, it can be achieved by thermochemical treatments, which include the thermal treatment of lignin in the presence or absence of some solvents, chemical additives and catalysts. Regarding with the yields and composition of degradation products, they vary based on the process type and conditions applied [4]. Aside from this fact, the nature of lignin, its composition and functional groups have important effects on the lignin conversion and products yields as well.

Efficiency of the lignin conversion process is defined in terms of conversion factors and yield values which means how much of the initial lignin has been successfully converted. In the simplest view, equation 3.1 can be used in order to calculate the lignin conversion factor [16].

$$\text{Conversion [wt \%]} = \frac{L_i - L_r}{L_i} 100 \quad (3.1)$$

In this equation, L_i represents the weight of the lignin input, and L_r is the weight of unreacted lignin which exists at the end of reaction.

3.1 Lignin Pyrolysis

Pyrolysis can be described as a thermal treatment of biomass or lignin in the absence of oxygen, with or without any catalyst. It is known that pyrolysis is the most studied method for biomass conversion thus far. In general, during pyrolysis process, molecular structure in the organic substance is broken down into smaller units [1]. The final products obtained from lignin or biomass pyrolysis will be solid, liquid,

and gas. Nevertheless, amount of these products changes depending on the severity of conditions applied, such as heating rate and reaction temperature. Solid product obtained at the end of pyrolysis process is called as char, and the yield of this product depends significantly on the pyrolysis temperature. For instance, it is indicated that the yield of this char is higher at lower temperatures [1].

Like biomass pyrolysis, pyrolysis of lignin is also very complex, and the major pyrolysis products of lignin consist of gaseous hydrocarbons with CO and CO₂, volatile liquids (methanol, acetone, and acetaldehyde), monolignols, monophenols (phenol, guaiacol, syringol, and catechol), and other polysubstituted phenols [1].

Lignin pyrolysis involves a rather wide range of temperatures in comparison to cellulose pyrolysis. Degradation of lignin starts with the weaker bonds cleavage at lower temperatures, and this process takes place through breaking of stronger bonds at higher temperatures, relatively. It is reported that at the temperatures higher than 500 °C, aromatic ring cracking and condensation occur [1].

In the first step, formic acid, formaldehyde, CO₂, CO and water are observed at the temperatures between 120-300 °C. It is believed that the cleavage of OH functional groups which are linked to β or α carbon in aliphatic side chains releases water, while breaking of the β-α carbon bonds in alkyl side chains releases formaldehyde [1]. As it is mentioned previously, it is relatively easier to break aryl ether linkages. On the other hand, however, ether linkages at α -carbons are more resistant. Even though, the general degradation tendency is similar, the yield of particular products and specific temperature for bond cleavage vary according to lignin type [1]. The major monomeric aromatics obtained from lignin pyrolysis are displayed in Figure 3.1.

3.1.1 Thermogravimetric pyrolysis studies

Ferdous et al. [17] reported experimental data for pyrolysis of alcell lignin and kraft lignin at different heating rates and temperatures up to 800 °C using a fixed bed microreactor. At a temperature of 800 °C, the gaseous product was mainly composed of H₂, CO, CO₂ and CH₄. It was observed that the overall conversion increases with increasing temperature. At lower temperatures, conversion is higher for lower heating rate. However, as the pyrolysis temperature increases, it starts to level off and, eventually, for temperatures above 700 °C conversion is higher for higher heating rates. They indicated that at 800 °C, conversion for allcel and kraft lignin

increased to 65 and 57 wt. % from 56 and 52 wt. %, respectively, when the heating rate was increased from 5 to 15 °C min⁻¹.

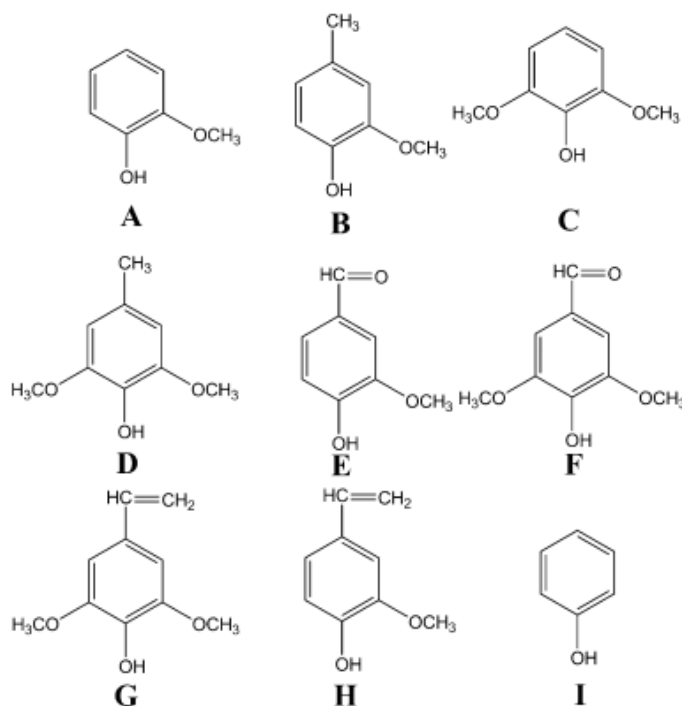


Figure 3.1 : Major products obtained from lignin pyrolysis: (A) guaiacol, (B) methyl guaiacol, (C) syringol, (D) methyl syringol, (E) vanillin, (F) syringaldehyde, (G) vinyl syringol, (H) vinyl guaiacol, (I) phenol [5].

Liu et al. [18] analyzed the pyrolysis products of strong acid detergent fiber lignin from birch and fir by using a thermogravimetric analyzer along with Fourier transform infrared spectrometry (TGA-FTIR). It was found that H₂O and CO₂ were the primary products at the temperatures around 100 °C. H₂O, CO, aldehydes, formic acid, and phenols were observed at around 225 °C. It was observed that the presence of CO₂ was more obvious in birch lignin, which indicates easier breaking of lateral chains. They remarked that a large quantity of monomeric phenols indicates the breakage of ether linkages at these temperatures. It was concluded that at temperatures around 425 °C for fir and 375 °C for birch, CO, CO₂, and hydrocarbons (mainly methane) became dominant. In this study, significant amounts of methanol were also observed.

3.1.2 Analytical pyrolysis studies

Alen et al. [19] performed an analytical pyrolysis of air-dried, bark free sawdust of Scots pine with 105-125 μm particle size. Pyrolysis was carried out at 300, 400, 600,

800, and 1000 °C at a heating rate of 1000 °C/s. It was reported that the main products occurred at 400 °C were phenolic aldehydes and alkylguaiacols, while at 600 °C phenolic aldehydes were converted into catechol and alkylphenols. They indicated that at higher temperatures (800 °C and 1000 °C) increase in aromatic hydrocarbons yield was observed, while phenolic aldehydes and guaiacols yields were considerably reduced.

3.1.3 Pyrolysis of lignin model compounds

As it is mentioned previously, the pyrolysis of lignin model compounds gives an idea to understand the thermal stability of the intermediate products formed during lignin pyrolysis.

Klein [20] studied the pyrolysis of guaiacol, which is known as dimeric lignin model compound, at 350 °C, and at the end of the experiments catechol, methane, phenol and carbon monoxide were observed as the main products. Klein indicated that catechol and methane yields were in almost stoichiometric amounts, as well as phenol and carbon monoxide. As proposed, demethylation of guaiacol yielded catechol. In addition, carbon monoxide and phenol were produced by demethoxylation of guaiacol. Also, he remarked that catechol yield was five times higher at 450 °C than at 300 °C.

Klein [20] also studied the pyrolysis of substituted phenols to determine the influence of the group functionalities on the thermal stability of the aromatic unit. In this study, syringol, isoeugenol, vanilin, anisole, benzaldehyde, veratrole, acetophenon, and cinnamaldehyde were pyrolysed at 300-500 °C in a small batch reactor. It is indicated that syringol and isogeugenol decomposed in a rather similar way as guaiacol. During the experiments, it was observed that substitution of guaiacyclic ring caused little influence on the pyrolysis mechanism of these compounds. Also, it is reported that anisole pyrolysis yielded a wider product spectrum than guaiacyclic model compounds. Considering veratrole pyrolysis, it behaved like anisole during its thermal decomposition. Guaiacol was observed as one of the major pyrolysis products; however it further decomposed to yield catechol and phenol. Moreover, compounds with carbonyl functionalities such as vanilin, benzaldehyde, acetophenone and cinnamaldehyde reacted mainly via decarbonylation. Vanilin showed higher reactivity compared to benzaldehyde, which

was attributed to electronic effects by methoxyl and hydroxyl substitutions in the aromatic ring. Comparison of acetophenone and benzaldehyde pyrolysis indicated that the terminal C=O groups (aldehyde) were more reactive than C=O groups in α - or β - positions (ketones). Furthermore, in the case of cinnamaldehyde pyrolysis, it yielded to phenol and alkylphenols.

Schlosberg et al. [21] suggested a possible pathway for the production of benzaldehyde, toluene, and phenol from anisole pyrolysis. In this study, phenol was produced by CH₃-O bond scission and further H-abstraction from anisole molecule. The free radical produced from the anisole underwent either rearrangement to benzaldehyde or stabilization to benzyl alcohol. It is indicated that this alcohol may further decompose to yield toluene and water.

Vuori and Bredenberg [22] studied the pyrolysis of guaiacol at 350-400 °C within the time range 0.5 to 4 h, and influence of tetralin as a hydrogen donor agent was evaluated as well. In their study, it was found that yields of catechol at 350 °C at reaction times from 0.5 to 2 h were similar. It was also indicated that catechol was formed at shorter times when the pyrolysis temperature was increased to 375 °C and 400 °C. At 375 °C, phenol was generated at the expense of catechol and o-cresol yields in the guaiacol pyrolysis. At 400 °C, catechol and phenol became predominant among the other products.

Masuku et al. [23] studied thermal decomposition of 4-propylguaiacol. The reaction temperatures were 350 °C and 375 °C, and reaction times from 20 to 120 min. In this study, high yield of 4-propylcatechol and methylpropylcatechol were obtained, and it was reported that methylpropylcatechol selectivity was higher at lower temperatures.

Lin et al. [24] studied the possible mechanism of wood liquefaction in phenol. They used a guaiacylglycerol- β -guaiacyl ether (GG) which is a dimeric lignin model compound. In this study, GG, phenol, and water in the weight ratio of 1:3:3 was heated in a 3 ml autoclave up to 120 min at 250 °C. Based on their results, liquefaction of GG in the presence of phenol produced low molecular weight intermediates which further reacted with phenol or with each other, and transformed to polymeric products. At the end of the experiments, more than 50 products were identified by GC/MS. According to the results of this experiment, guaiacol and variety of dimmers were the main products of GG thermal degradation. It was

indicated that production of phenol was related to the consumption of GG. It was also suggested that guaiacol was derived directly from the cleavage of β -O-4 linkages.

Simmons and Klein [25] reported a study of the degradation mechanism of lignin pyrolysis. In this study, dibenzyl ether (DBE) was chosen as a model compound, and deuterated tetralin was used for the DBE pyrolysis to monitor the amount of deuterated toluene, which indicates the operating pyrolysis mechanism. As to the pyrolysis product composition and kinetics, three possible mechanisms were cited for its thermal degradation: a free radical mechanism, a concerted reaction, and a combined concerted free radical reaction. According to their results, 87 % of the toluene produced by DBE pyrolysis was partly deuterated, so that the free radical mechanism was predominant over the concerted reaction.

Klein [20] investigated the pyrolysis of five different dimeric lignin model compounds to simulate the interunit C-C and C-O bonds thermal behavior. He used phenethyl-phenyl ether as a model compound to simulate β -ether linkages in lignin in the pyrolysis process, and other ether linkages were represented by other model compounds such as benzyl phenyl (α -ether bond), phenyl ether (C-O bonds), biphenyl (C-C bonds) and biphenol (C-C bonds). Pyrolysis of phenethyl-phenyl ether yielded phenol, styrene, toluene, and alkyl benzene. It was remarked that these products were formed by the rupture of the ether bonds and the alkyl side chain. It was also indicated that phenol and styrene were the primary pyrolysis products from β -ether bond cleavage.

3.2 Hydrogenolysis/Hydrogenation

Pyrolysis is not a natural choice for converting lignin into liquid fuel or chemicals as it mainly results in solid coke and gas. However, pyrolysis may be performed in the presence of hydrogen, and this process being known as hydrogenolysis.

Hydrogenolysis is one of the most promising approaches to lignin depolymerization as the yields of monomer products are usually higher and product mixtures generally simpler than those produced via other degradation methods. Hydrogenolysis leads to higher net conversion, higher yields of monophenols, and less char formation. Also, application of suitable solvents and catalysts can speed up the reaction and increase

the product yield [5]. Hydrogenation is performed either by treating lignin in an active hydrogen-donating solvent, or in gaseous hydrogen.

3.2.1 Base-catalyzed depolymerization

Catalysts have been considered an important input for the lignin conversion processes. Catalysts are used in lignin depolymerization to promote high conversion ratios, and suppress char formation and condensation, while keeping the reaction severity under a permissible limit. On the other hand, one of the most important aims of catalyst utilization is to achieve selective bond cleavage, leading to high selectivity values for a particular compound in the product stream. Catalysts have been tested for processes and substrate including both model compounds and lignin extracts so far [5].

Lercher et al. [26] studied the benzyl phenyl ether conversion in superheated water in the presence of alkali carbonates such as LiCO_3 , Na_2CO_3 , and K_2CO_3 within the temperature range 270 – 370 °C. They mainly observed phenol and benzyl alcohol, and a large amount of consecutive product depending on the operating conditions. It is indicated that high selectivity towards hydrolysis can be achieved at lower temperatures and short reaction times. Under more severe conditions, the yields of phenol and especially benzyl alcohol decrease and higher molecular weight compounds form by consecutive reactions. It was remarked that the yields of toluene, 2 and 4-benzyl phenol are strongly enhanced in the presence of alkali carbonate.

Thring [27] studied the alkaline degradation of alcell lignin, a type of organosolv lignin. He used a 500 ml stainless steel reactor, and carried out the reactions at temperatures between 200 °C and 340 °C for 15 to 90 minutes. The concentrations of NaOH solutions were starting from 0.5 wt% to 6 wt% for both in water and in ethanol. According to results obtained, temperature was more important than the reaction time. Maximum yield of DCM-solubles was noted to be at 10 % of the lignin fed to the reactor, with a maximum of 4 wt % identified and quantified monomeric products.

Miller et al. [28] published a study on BCD using lignin and lignin model compounds in a microreactor. In this study, organosolv lignin and lignin model compounds such as anisole, guaiacol, phenyl ether, biphenyl, and benzyl phenyl ether were reacted with 10 % KOH and ethanol or methanol at 290 °C for reaction

times up to 1h. Kinetic studies showed that BCD is a fast reaction and occurs within 15 min. They reached highest conversion with organosolv lignin, and ethanol showed better performance than methanol as solvent. Also, the analysis of products from model compounds revealed that phenyl ether linkages were effectively broken in the BCD reaction while carbon-carbon linkages were less affected.

Shabtai et al. [29] reported a study on BCD followed by hydrodeoxygenation and hydrocracking. In this study, a three-step process for converting lignin into reformulated gasoline was proposed. The base-catalyzed depolymerization was carried out at 270 °C, and in the presence of autogenous pressure which was around 140 bar for 1-5 min. BCD resulted in depolymerized lignin mono-cluster compounds with about 50 % decrease in oxygen content. In the second step, depolymerized lignin was subjected to hydrodeoxygenation in the presence of catalyst such as sulfided CoMo/Al₂O₃. In the final stage, partial ring hydrogenation was applied in order to obtain final product comparable to reformulated hydrocarbon gasoline.

3.2.2 Hydrogen-donating solvents

It is known that some solvents are able to modify the thermal degradation mechanism, promoting the production of specific hydrocarbons. In particular, solvents with hydrogen donor capability such as tetralin and decalin are able to terminate the chain reactions by giving hydrogen to the molecules. Although the effect of hydrogen donor solvents has been extensively investigated for coal liquefaction, just a few works dealt with the thermal degradation of lignin using this type of solvents.

Thring et al. [30] studied the effects of severity on conversion using hardwood solvolytic lignin, and tetralin as a solvent. They observed that maximum conversion was 68 % and char formation was low in all cases. It was indicated that conversion was essentially constant for low values of mass ratio (ratio of lignin to the sum of lignin and tetralin), however it was decreased for higher ratios. It was also remarked that conversion decreased if the amount of hydrogen donating solvent decreased. According to the results of this study, the decomposition products showed a similar trend with pyrolysis products.

Kudsy et al. [31] reported a study on a lignin hydrogenolysis in the presence of tetralin as a solvent. They found that amount of phenolic compounds increased while

addition of tetralin increased. However, they indicated that amount of tetralin did not play important role on the gaseous product yield.

Kleinert and Barth [3] published a study on lignin depolymerization in the ethanol as a reaction medium, and in the presence of formic acid as hydrogen donor. During the process, both depolymerization and removal of oxygen by formation of water were observed. They indicated that liquid product yield was improved by using alcohol as a solvent, and very little coke formation (% 5) was reported. The liquid produced comprise two easily separable phases, where the lighter organic phase consist of mainly low molecular weight alkylphenols and C₈-C₁₀ aliphatics.

3.2.3 Hydrodeoxygenation

Hydrodeoxygenation is a catalytic way to remove oxygen in the presence of H₂ at elevated temperatures. It is known that the other catalytic treatments have been traditionally used already in petroleum refining to remove the compounds which may have debilitating effects on the downstream processing catalysts, and hydrodeoxygenation was not used as much as the other applications since oxygen is not a major component of fossil fuels. However, regarding with oxygen content of biomass, hydrodeoxygenation becomes a necessity to be able to produce petroleum-compatible bioderived alternatives as it contains more than 40 % oxygen [8].

Lercher et al. [32] reported a study on an aqueous phase catalytic hydrodeoxygenation of bio-derived phenols. In their study, dual-functional catalyst system Pd/C and H₃PO₄ is used in order to better understand the elementary steps of the overall conversion. They indicated that the reaction proceeded via stepwise hydrogenation of the aromatic ring, transformation of the cyclic enol to the corresponding ketone, hydrogenation of the cycloalkanone to the cycloalkanol and its subsequent dehydration as well as the hydrogenation of the formed cycloalkene. They remarked that the presence of dual catalytic functions was indispensable for the overall hydrodeoxygenation.

Lercher et al. [33] published a study on a hydrodeoxygenation of bio-derived phenols by using RANEY[®] Ni and Nafion/SiO₂ catalysts. They showed that the conversion of phenols to hydrocarbons and methanol was achieved with nearly 100 % yields.

Wild et al. [34] studied hydrotreatment of pyrolytic oil obtained from pyrolytic depolymerization of lignin. In this study, molecular hydrogen at 10 MPa was used to

react with pyrolytic oil at 350 °C for 1 h in the presence of Ru/C catalyst. At the end of the experiments, Cycloalkanes and alkyl-substituted cyclohexanols were observed as dominant fractions in the product.

Meier et al. [35] performed a catalytic hydrogenolysis of lignin with gaseous hydrogen in the presence of NiMo aluminosilica catalyst. They obtained liquid oil yielded of around 65 wt %. It is indicated that the partial hydrogen pressure has a significant effect on the conversion.

Oasmaa and Johansson [36] worked on kraft lignin conversion in the presence of hydrogen gas at 10 MPa and a water-soluble molybdenum catalyst. They reported that the presence of hydrogen suppressed the char formation.

Thring and Breau [37] observed in their study that addition of hydrogen to a pressure of 1 MPa increased the net conversion, reducing the residue from 40 wt % to 11 wt %.

Keane et al. [38] worked on the phenol hydrodeoxygenation using a glass reactor in the presence of silica catalyst, under H₂ flow, and in the temperature range 423 – 573 K. They varied the H₂ flow rate and reaction medium. According to results from this study, cyclohexanol was observed as a main product, followed by benzene and cyclohexanone.

Hong et al. [39] reported hydrodeoxygenation of aqueous phenol (10 wt % water) at elevated pressures (40 bars) at 200 °C using Pt supported on different supports, but mainly on zeolite HY (0.5 wt % Pt/HY). Due to the presence of the acidic support, the main product in these experiments was cyclohexane.

3.2.4 Solvents in supercritical conditions

Depolymerization of lignin can be achieved by using supercritical solvents. Solvents in supercritical conditions behave differently than in subcritical conditions, and have many interesting advantages. Until now, lignin and lignin model compounds have been studied in supercritical water ($T_c = 374.15$ °C and $P_c = 22.1$ MPa) by researchers, and these studies have shown that lignin can be converted into smaller monomeric units. However, yields of monomeric phenols have been lower than expected, probably due to repolymerization of monomers [10].

Xu et al. [7] published a study on Jack pine wood powder within the reaction medium of sub-/super-critical solution of ethanol at temperature of 473 – 623 K, and in the presence of H₂ varying from 2.0 to 10.0 MPa. In this study, Iron-based catalysts (FeS or FeSO₄) were selected. They observed the oil yields generally increased (17 % to 44 %) with increasing residence time, and phenolic compounds were the dominant compounds detected in the oils. Also, they remarked that the addition of iron-based catalysts significantly enhanced both production of oils and biomass conversion.

Tsujino et al. [40] reported a study of lignin model compounds in supercritical methanol (250-270 °C, 24-27 MPa) at the tin bath temperature of 270 °C with a batch type vessel. Guaiacol and veratrole were selected as guaiacyl type of aromatic ring in lignin, while 2, 6-dimethoxyphenol and 1, 2, 3-trimethoxybenzene as a syringyl. In addition, biphenyl and β -O-4 types of dimeric lignin model compounds were, respectively, studied as condensed and ether linkages between C₆-C₃ phenyl propane units. As a result, they observed that both guaiacyl and syringyl types of aromatic rings were very stable. However, β -ether linkage in the phenolic β -O-4 model compound was cleaved rapidly into guaiacol and coniferyl alcohol.

Lü et al. [41] worked on conversion of benzyl phenyl ether in high temperature liquid water. Benzyl phenyl ether was treated at temperatures ranging from 220 to 250 °C. It is shown that BPE undergoes hydrolysis in HTWL, and main products were found as phenol and benzyl alcohol with the minimum selectivities of 75.7 % and 82.8 %, respectively. Lower temperature led to higher selectivity in 220 – 250 °C temperature range. The kinetics on BPE hydrolysis was investigated, and the activation energy was determined as 150.3 ±12.5 kJ/mol with the first-order kinetic equations.

4. EXPERIMENTAL

4.1 Chemicals

In this research, chemicals were obtained from Sigma-Aldrich and were used without further purification. These chemicals are diphenyl ether (99%), benzyl phenyl ether (98%), diphenyl methane (99%), biphenyl (99%), phenol (99%), cyclohexanol (99%), cyclohexanone (99%), cyclohexene (99%), cyclohexane (99.5%), benzene (99.8%), toluene (99.8%), cyclohexanemethanol (99%), bicyclohexyl (99%), ethylcyclohexane (99%), cyclohexyl phenyl ether (95%), benzaldehyde (99%), benzyl alcohol (99.8%), Pt/C (5 wt.%), Ru/C (5 wt.%), and Ru/Alumina (5 wt. %).

4.2 Experimental Setup

The bench scale hydrogenolysis experiments were carried out by using a 12-ml stainless steel Swagelok autoclave reactor. The experimental unit consists of autoclave reactor, electrical heater, stirrer, and thermocouple for measuring the temperature of the reactor. Experimental setup is shown in Figure 4.1.



Figure 4.1: Experimental setup.

4.3 Experimental Procedure

4.3.1 Dimeric lignin model compound experiments

In a typical run of normal case, dimeric lignin model compound (0.795 mmol), 5 wt. % Pt/C catalyst (5 mg), and H₂O (6 mL) as a reaction medium were added to an autoclave reactor. Then, reactor was sealed, and H₂ loading to autoclave reactor step took place. After purging the reactor 3 times with H₂, the reaction was carried out with 20 bar H₂ (room temperature) at 200 °C for different reaction times such as 0.5 h, 1 h, 2 h, and 4 h at stirring speed of 1000 rpm. After the reaction was halted, the reactor was quickly cooled down to room temperature in order to prevent further polymerization reactions. Ethyl acetate was used to extract the organic mixture from aqueous solution, and organic phase was then analyzed by GC/MS and GC/FID.

In a typical run of acid case, the experimental procedure mentioned above was followed in the presence of 0.5 wt %, H₃PO₄/H₂O (6 mL) for dimeric lignin model compound experiments.

4.3.2 Phenol experiments

As to monomeric lignin model compound phenol hydrodeoxygenation experiments, different type of commercial catalysts such as Pt/C (5 wt. %), Pt/C (5 wt. %, reduced at 600 °C), Pt/C (5 wt. %, reduced at 800 °C), Ru/C (5 wt. %), and Ru/Alumina (5 wt. %) were performed.

In a typical test, phenol (1.59 mmol), 5 wt. % Pt/C (5 mg), 5 wt. % Pt/C (reduced at 600 °C, 5 mg), 5 wt % Pt/C (reduced at 800 °C, 5 mg), 5 wt. % Ru/C (2.7 mg), 5 wt. % Ru/Alumina (2.6 mg), and H₂O (6 mL) as a reaction medium were added to an autoclave reactor. After that, reactor was sealed, and H₂ loading to autoclave reactor step took place. After purging the reactor 3 times with H₂, the reaction was carried out with 20 bar H₂ (room temperature) at 200 °C for different reaction times such as 0.5 h, 1 h, 2 h, and 4 h at stirring speed of 1000 rpm. After the reaction was halted, the reactor was quickly cooled down to room temperature in order to prevent further polymerization reactions. Ethyl acetate was used to extract the organic mixture from aqueous solution, and organic phase was then analyzed by GC/MS and GC/FID.

In a typical run of acid case, phenol hydrodeoxygenation experiment was performed for 5 wt. % Pt/C catalyst in the presence of 0.5 wt % H₃PO₄/H₂O (6 mL).

4.4 Analyses

4.4.1 Transmission electron microscopy (TEM)

Transmission Electron Microscopy (TEM) instrument was used to see particle size distributions of Pt/C catalysts. In this respect, transmission electron micrographs were acquired on FEI Technai 20 transmission electron microscope at an acceleration voltage of 200 kV with a LaB6 filament (see Figure 4.2). Typically, a small amount of grinded commercial Pt/C (5 wt. %) samples were reduced at 600 °C and 800 °C with 25 vol. % H₂ in He for 2 h before being suspended in pure ethanol, sonicated and dispersed over a Cu grid with a holey carbon film. TEM images were recorded using a CCD camera at different magnifications. From the electron micrographs, the particle size was determined assuming that the particles are spherical.



Figure 4.2: FEI Technai 20 transmission electron microscope.

4.4.2 Gas chromatography-mass spectroscopy (GC/MS)

GC/MS measurements were performed to detect the lignin model compounds and dimeric or monomeric products occurred during hydrogenolysis reactions. Liquid samples obtained at the end of the bench scale experiments were analyzed by using a “Shimadzu” GC17A/GCMS-QP 5050A instrument (see Figure 4.3). Gas

chromatograph was used to separate the organic mixture vapors, and Restek Rxi-5ms capillary column which has 30 m length, 0.25 mm diameter with 0.25 μm thickness was used to analyze the products. The data was processed with “GCMS solution” software provided by Shimadzu.



Figure 4.3 : Shimadzu GC17A/GCMS-QP 5050A.

4.4.3 Gas chromatography-flame ionization detector (GC/FID)

GC/FID measurements were performed to quantify the lignin model compounds and dimeric or monomeric products occurred during hydrogenolysis reactions. Liquid samples obtained at the end of the bench scale experiments were analyzed by using a “Interscience” Focus GC (FID detector) instrument with a Restek Rxi-5ms capillary column (see Figure 4.4). This column has 30 m length, 0.25 mm diameter with 0.25 μm thickness.

The concentrations of the lignin model compounds as well as the dimeric or monomeric products occurred during hydrogenolysis reactions were determined by calibrating the peak area with ethyl acetate solutions of known concentration of these compounds.

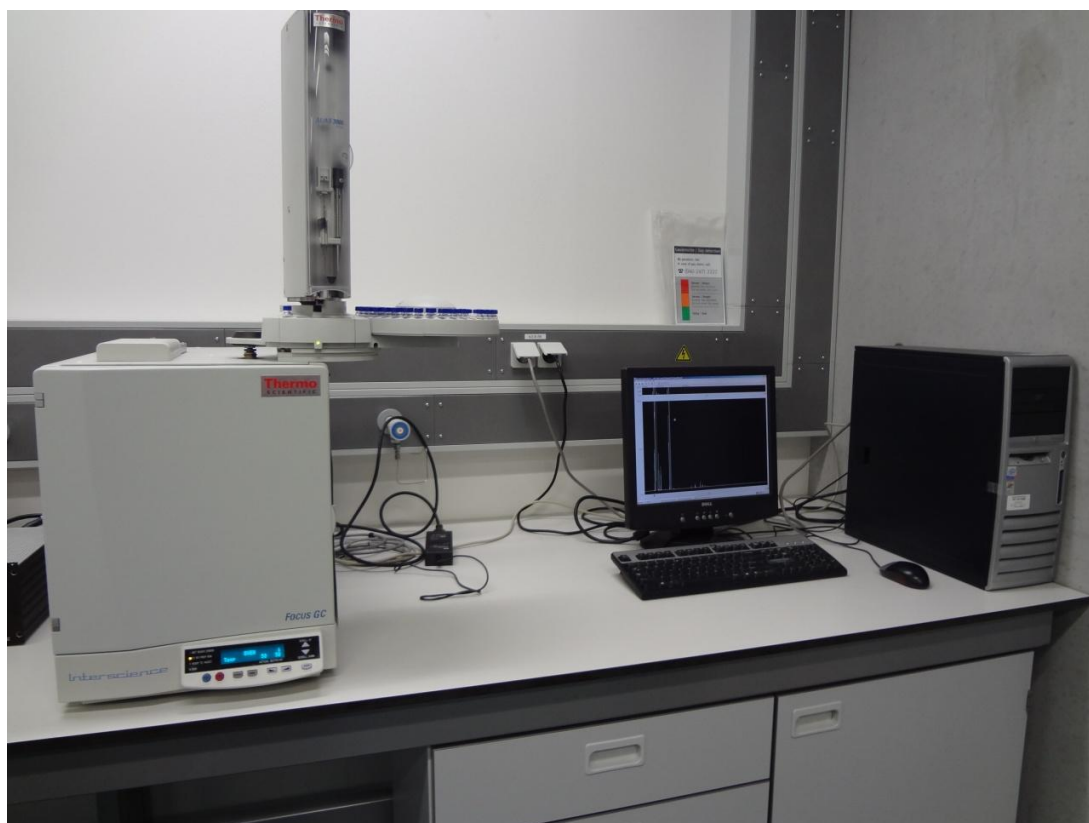


Figure 4.4 : Interscience Focus GC (FID detector).

The GC method developed and used for the product analysis was carried out under conditions given in Table 4.1.

Table 4.1 : GC method applied for model compound experiments.

Model compound experiments	
Column oven temperature	50 °C
Injection temperature	230 °C
Injection mode	Split
Column flow	1.5 mL/min
Signal range	10
Split flow	75 mL/min
Split injection ratio	50
Carrier gas	Helium
Initial temperature of oven	50 °C
Final temperature of oven	300 °C
Heating rate	20 °C/min

Retention times of calibrated model compounds and products from lignin model compound experiments are shown in Table 4.2.

Table 4.2 : Retention times of calibrated model compounds and products from model compound experiments.

Compound	Chemical formula	Retention time [min]
Cyclohexane	C ₆ H ₁₂	1.95
Benzene	C ₆ H ₆	2.01
Cyclohexene	C ₆ H ₁₀	2.04
Toluene	C ₇ H ₈	2.44
Ethylcyclohexane	C ₈ H ₁₆	2.84
Cyclohexanol	C ₆ H ₁₂ O	3.18
Cyclohexanone	C ₆ H ₁₀ O	3.26
Benzaldehyde	C ₇ H ₆ O	3.74
Phenol	C ₆ H ₆ O	3.82
Cyclohexanemethanol	C ₇ H ₁₄ O	4.08
Benzyl alcohol	C ₇ H ₈ O	4.30
Bicyclohexyl	C ₁₂ H ₂₂	6.37
Biphenyl	C ₁₂ H ₁₀	6.86
Diphenyl ether	C ₁₂ H ₁₀ O	6.98
Cyclohexyl phenyl ether	C ₁₂ H ₁₆ O	7.14
Diphenyl methane	C ₁₃ H ₁₂	7.20
Benzyl phenyl ether	C ₁₃ H ₁₂ O	8.03

5. RESULTS AND DISCUSSION

5.1 Characterization of Pt/C Catalyst by using Transmission Electron Microscopy (TEM)

TEM analyses were made in order to see the dispersion of platinum particles and particles sizes of it on activated carbons. TEM images and the corresponding histograms of the particle size distributions are given in Figures 5.1, 5.2, and 5.3. It can be seen from these figures that average particle size depends on the reduction conditions. From the particle size distribution graph shown in figure 5.1 it was observed that untreated commercial Pt/C catalyst presents particle sizes mainly between 1.5 and 2.5 nm, and a few particles lower than 1.5 nm were detected. However, considering Pt/C catalyst reduced at 600 °C, it is observed from Figure 5.2 that most frequently found particle sizes are between 2.75 and 3.25 nm. Regarding with Pt/C catalyst reduced at 800 °C, TEM analyses show presence of not only particles in the range of 3-4 nm, but also a fair amount of larger particles (see Figure 5.3). On the other hand, it is also possible to see a significant number of well defined particles. This observation suggests that metals are well-dispersed on the support.

From the TEM micrographs it can be concluded that reduction at different temperatures lead to reasonable changes in the average particle size. As it can be seen in the histograms, an increase in the reduction temperatures causes an increase in the particle size of the crystallites. These results are in an agreement with those reported by Sepulveda-Escribano et al. [42] for Pt supported on activated carbons. These authors observed that reduction at higher temperatures originates a decrease in the dispersion, which should be attributed to an increase in the metallic particle size due to the migration of particles and sintering during the reduction steps.

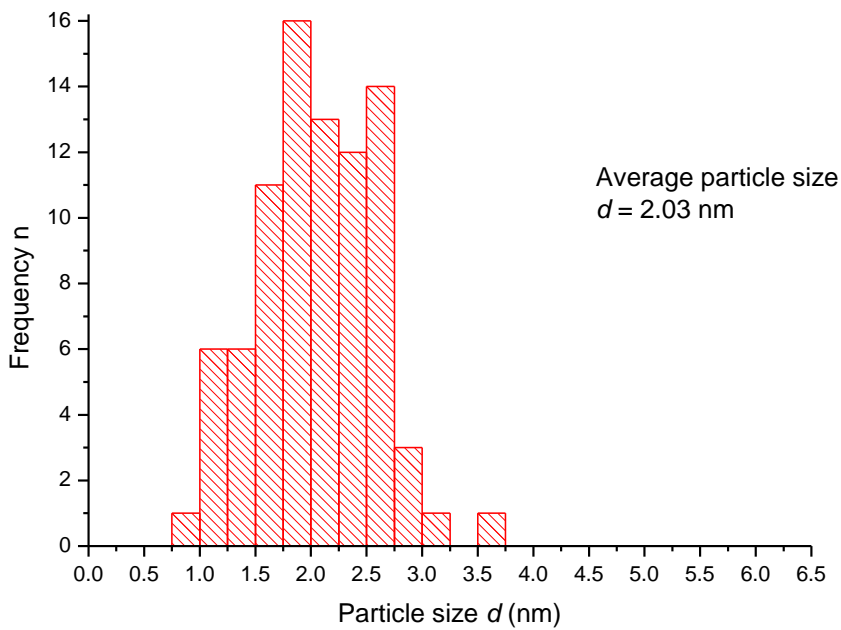
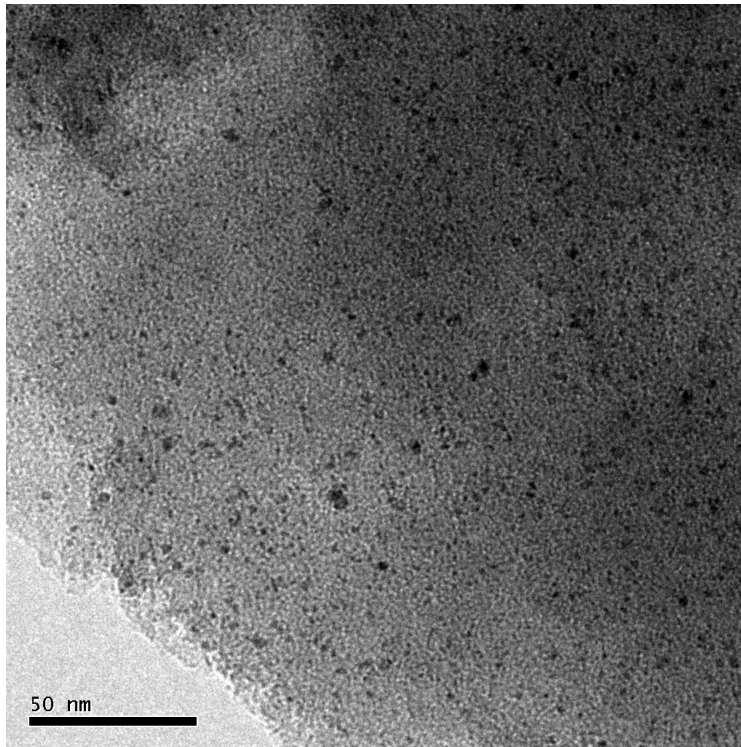


Figure 5.1 : TEM micrograph and particle size distribution of commercial 5 wt. % Pt/C catalyst.

The increase of the particle size can also be promoted by thermal decomposition of the oxygenated surface groups initially presented on the activated carbon surface. With the destruction of these groups, the fixed small metal particles would become mobile on the surface, and therefore would agglomerate to larger particles [43].

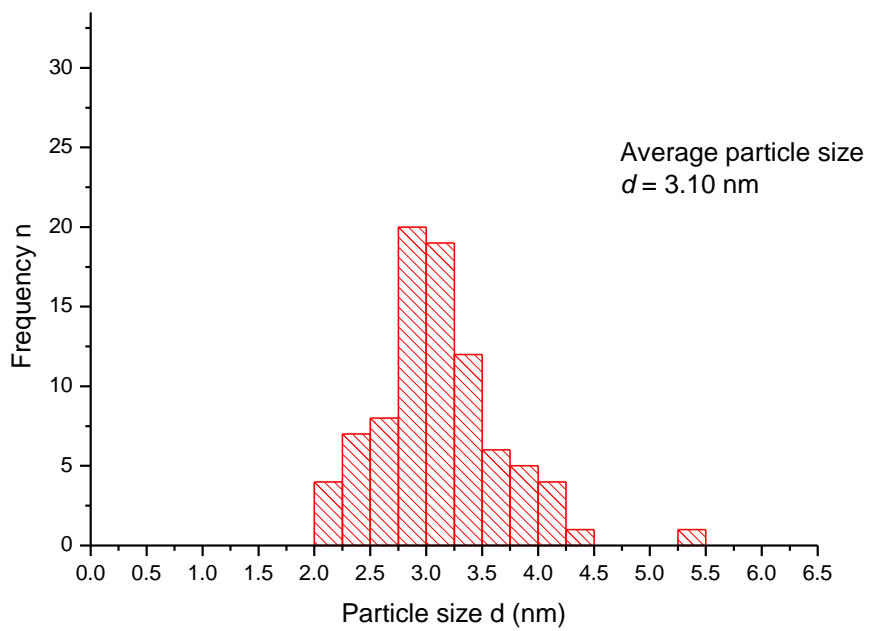
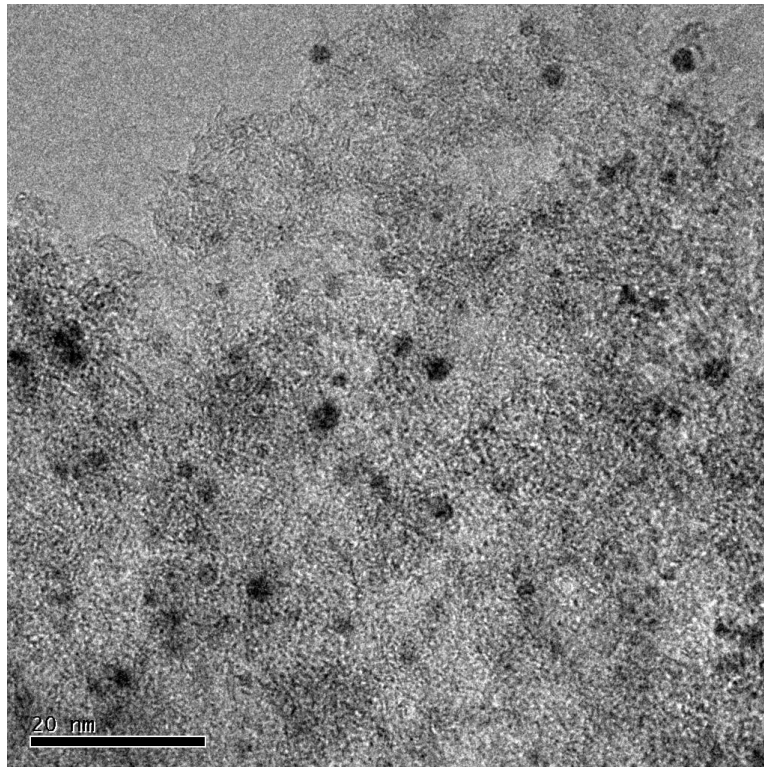


Figure 5.2 : TEM micrograph and particle size distribution of commercial 5 wt. % Pt/C catalyst reduced at 600 °C.

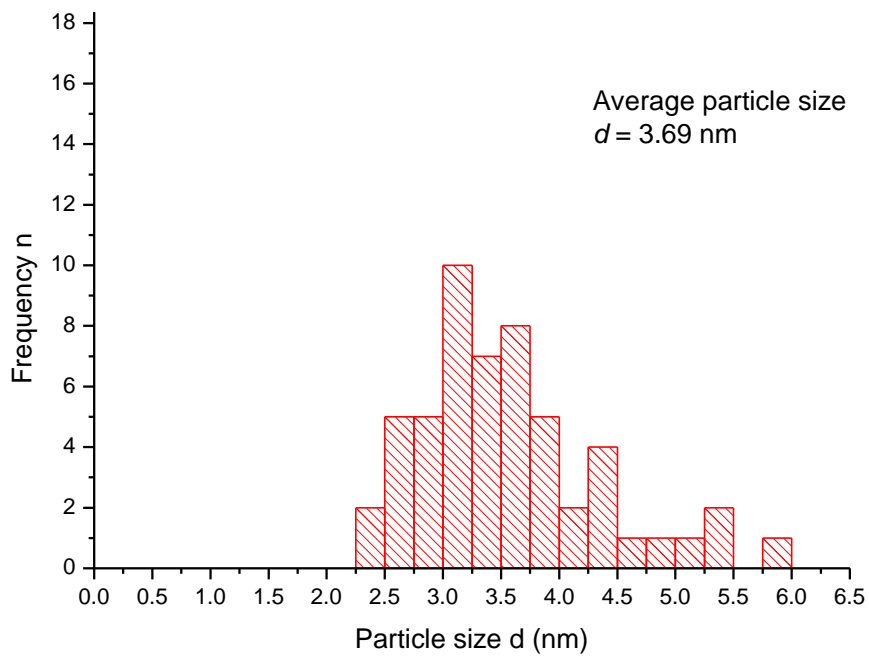
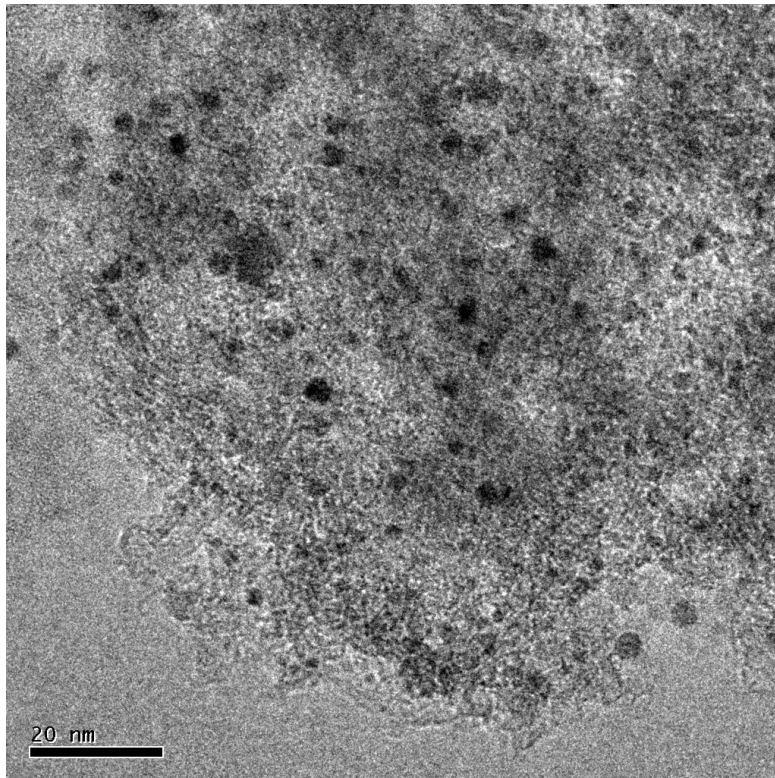
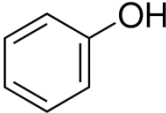


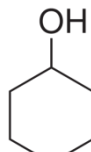
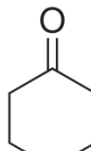
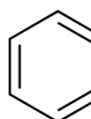


Figure 5.3 : TEM micrograph and particle size distribution of commercial 5 wt. % Pt/C catalyst reduced at 800 °C.

5.2 Phenol Hydrodeoxygenation

In order to explore the principal chemistry in the aqueous-phase hydrodeoxygenation, phenol was selected as the model compound. The main product obtained from the aqueous-phase hydrodeoxygenation of phenol is light and colorless oil. GC/MS and GC/FID measurements show that it contains monomers. Table 5.1 summarizes the main monomeric components and their chemical structures obtained from phenol hydrodeoxygenation experiments.

Table 5.1 : Monomeric components obtained in the oil from phenol hydrodeoxygenation experiments.

Monomer	Chemical Formula	Structure
Phenol	C_6H_6O	
Cyclohexene	C_6H_{10}	
Cyclohexane	C_6H_{12}	
Cyclohexanol	$C_6H_{12}O$	
Cyclohexanone	$C_6H_{10}O$	
Benzene	C_6H_6	

5.2.1 Phenol hydrodeoxygenation in the presence of commercial Pt/C catalyst

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Pt/C catalyst in order to see phenol conversion and distribution of

products obtained at the end of reactions. Figure 5.4 plots the conversion of phenol and selectivity of products occurred during the reactions versus reaction time.

In the light of experimental findings, in neutral water under conditions of 200 °C and 20 bar H₂, nearly 100 % phenol conversion was achieved in 1h (see Figure 5.4). This is expected due to the catalyst activity under these reaction conditions. It is known from literature that Pt/C catalyst favors the phenol conversion with high yields at the temperature around 200 °C [32].

In addition to this, under the same reaction conditions the selectivity to cyclohexanol increased almost linearly with increasing phenol conversion, and Pt/C yielded to 61 % cyclohexanol in 0.5 h, then it was reached to 98 % at the end of the 4 h (see Figure 5.4). This is also expected since the high hydrogen pressure, high temperature and strong adsorption of phenol on carbon lead to cyclohexanol being the dominant component among the products [44].

On the other hand, It can be seen from Figure 5.4 that cyclohexanone is appeared as intermediate product along with the reaction. This result is in accordance with those reported by Lercher et al. [45] and Jones et al. [39]. Considering the cyclohexanone formation and consumption during the reaction, these authors suggest that phenol is hydrogenated to cyclohexanone in the first step, and therefore cyclohexanone may appear as an intermediate in the isomerization of partial-hydrogenation product cyclohexenol (cyclic keto/enol transformation), afterwards cyclohexanone hydrogenated to cyclohexanol with the hydrogenation catalyst (see Figure 5.5).

Besides, it can also be seen from Figure 5.4 that traces of cyclohexene and cyclohexane were detected during the reaction. Even though this finding has not been reported under non-acidic conditions for Pt/C catalyst, it is known from literature that under various reaction conditions using different catalysts, some authors observed cyclohexene and cyclohexane formation, and suggested that cyclohexanone could directly be hydrogenated to cyclohexene and cyclohexane [39]. Other possible explanation for the formation of these compounds is given in literature by Talukdar et al. [46]. These authors suggest that partial hydrogenolysis of phenol is responsible for, yielding benzene, cyclohexene, and cyclohexane. The possible reaction pathway of phenol to monocyclics is shown in Figure 5.5.

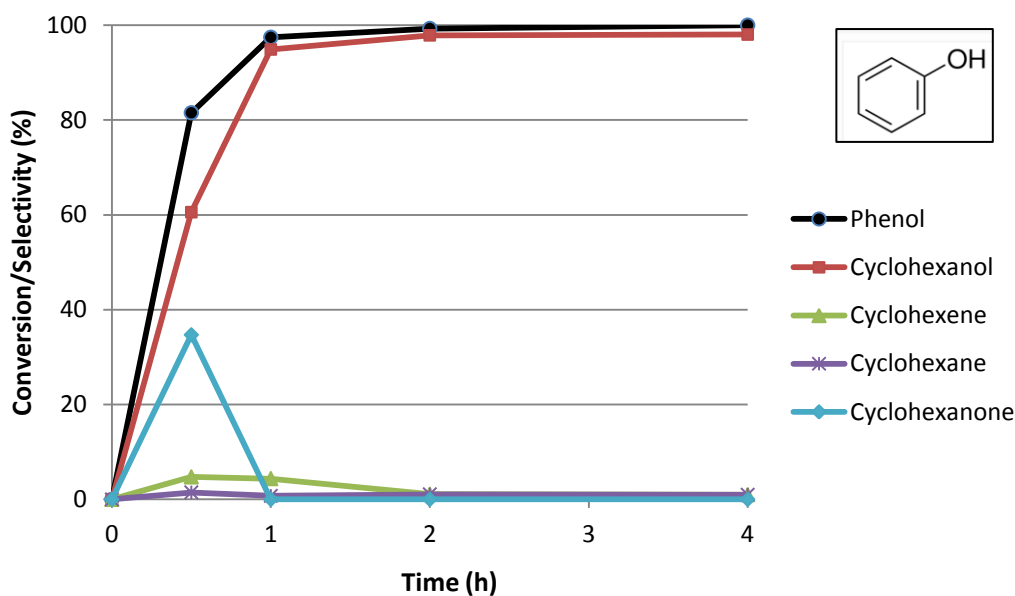


Figure 5.4 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Pt/C catalyst.

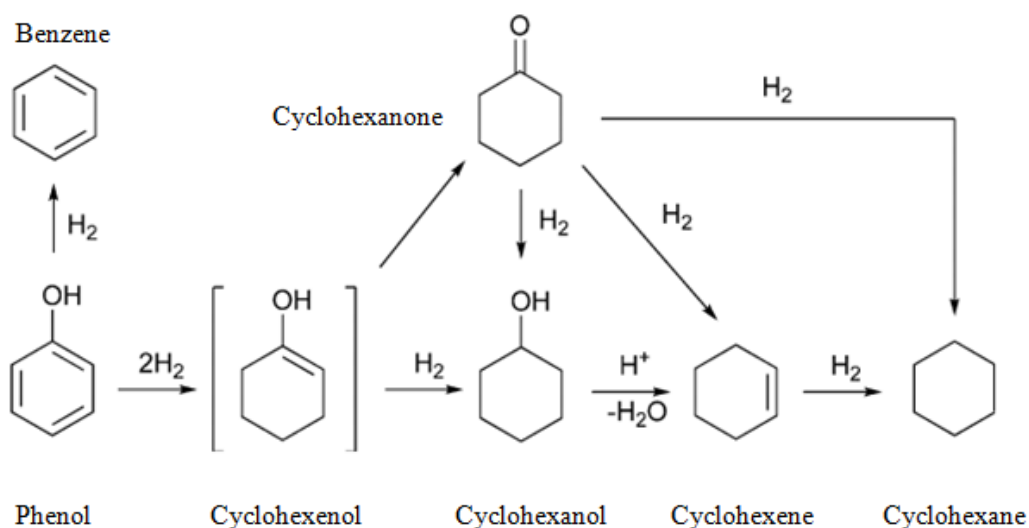


Figure 5.5 : Reaction pathway of phenol to monocyclics in the catalytic hydrogenation treatment [39].

5.2.2 Phenol hydrodeoxygenation in the presence of commercial Pt/C catalyst and H_3PO_4

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Pt/C catalyst and 0.5 wt. % phosphoric acid (H_3PO_4) in order to see phenol conversion and distribution of products obtained at the end of reactions. Figure 5.6 plots the conversion of phenol and selectivity of products occurred during the reactions versus reaction time.

According to these experimental findings, it can be seen from this figure that nearly 100 % phenol conversion was achieved in 1 h as it is expected. However, it is important to report that the product distribution was significantly changed when phosphoric acid introduced to reaction medium. Applying phosphoric acid led to 77 % cyclohexane selectivity in 1 h, and it was reached to 96 % at the end of 4 h. It is known from literature that formation of cyclohexane from phenol requires bifunctional catalyst [44, 45], and presence of hydronium ions for dehydration at a proper temperature and metallic function able to hydrogenate in the presence of water.

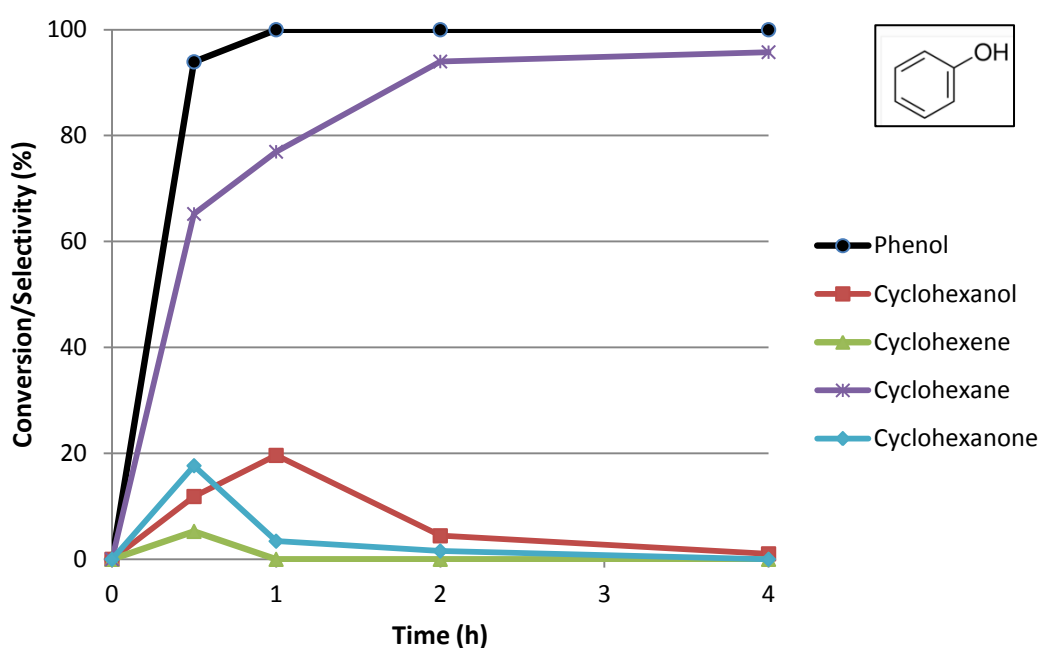


Figure 5.6 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Pt/C catalyst and H_3PO_4 .

As it can be seen from Figure 5.5 that the overall reaction pathway for aqueous-phase hydrodeoxygenation of phenol to cyclohexane starts with an initial metal-catalyzed hydrogenation of aromatic ring, and then followed by acid-catalyzed dehydration of cyclohexanol and metal-catalyzed hydrogenation of cycloalkene.

As to cyclohexanone distribution, it was obtained at the beginning of the reaction with the selectivity of 18 % in 0.5 h, and proceeded with a decreasing trend. It was totally consumed in 2h, and it can be said that cyclohexanone appeared as an intermediate as it is expected.

On the other hand, cyclohexanol selectivity increased up to 20 % in 0.5 h as phenol conversion increased, however it started to decrease after 0.5 h passed, and was totally consumed in 4 h. This is expected due to the fact that cyclohexanol is converted to cyclohexane in the presence of acidic site.

5.2.3 Phenol hydrodeoxygenation in the presence of commercial Pt/C catalyst reduced at 600 °C

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Pt/C catalyst reduced at 600 °C in order to monitor Pt particle size effect on catalytic activity for phenol conversion and distribution of products obtained at the end of reactions. Figure 5.7 illustrates the phenol conversion and selectivity of products occurred during the reactions versus reaction time.

Experimental findings showed that in neutral water under conditions of 200 °C and 20 bar H₂, phenol conversion is decreased from 97 % to 76 % in 1 h, and from 100 % to 86 % at the end of 4 h compared to untreated commercial Pt/C catalyst (see Figures 5.4 and 5.7). Also, it can be seen from these figures that selectivity of cyclohexanone is decreased from 35 % to 13 % in 0.5 h. On the other hand, it is observed that selectivity of cyclohexanol remained almost the same in the cases of treated and untreated Pt/C catalysts.

Therefore, it can be reported that increasing the mean Pt particle size from 2.03 nm to 3.10 nm caused an activity loss for phenol conversion. However, it can be remarked that it does not show decreasing effect on cyclohexanol selectivity as phenol conversion decreases. The activity loss of Pt particles can be explained by the fact that the Pt surfaces were modified during the calcination step. As it is already known that the surface area of Pt particles was decreased as the particle size was increased, and therefore the surface specific activity of Pt was decreased.

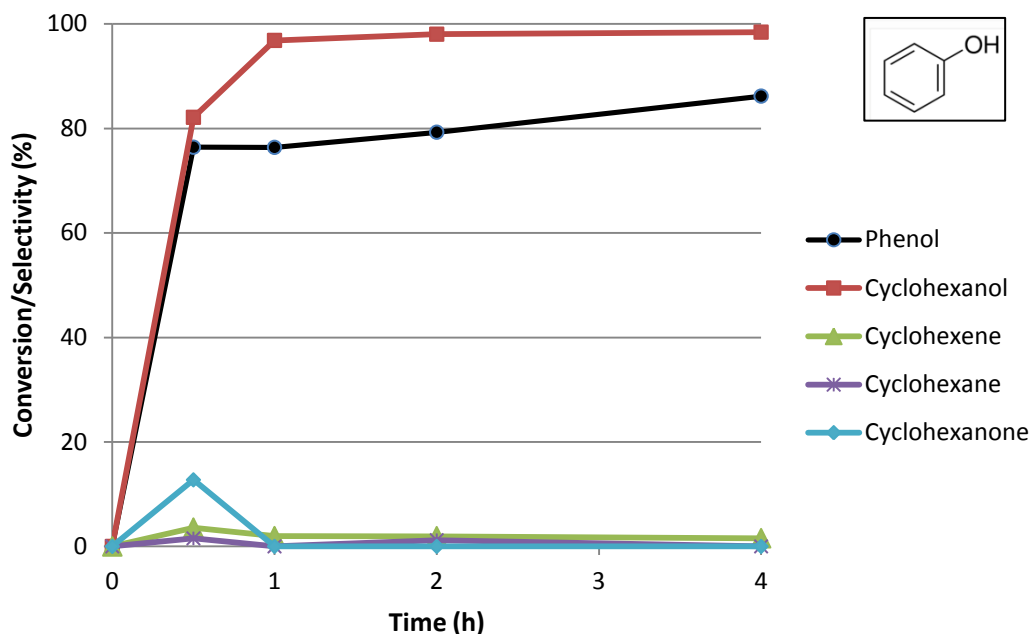


Figure 5.7 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Pt/C reduced at 600 °C.

5.2.4 Phenol hydrodeoxygenation in the presence of commercial Pt/C catalyst reduced at 800 °C

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Pt/C catalyst reduced at 800 °C in order to monitor Pt particle size effect on catalytic activity for phenol conversion and distribution of products obtained at the end of reactions. Figure 5.8 shows the conversion of phenol and selectivity of products occurred during the reactions versus reaction time.

In neutral water under conditions of 200 °C and 20 bar H₂, it can be seen Figure 5.8 that phenol conversion is decreased from 97 % to 82 % in 1 h, and from 100 % to 88 % at the end of 4 h compared to untreated commercial Pt/C catalyst (see figures 5.4 and 5.8). On the other hand, it is important to report that in the presence of Pt particles, that has 3.69 nm particle sizes; cyclohexanone appeared more stable under the reaction conditions, and therefore cyclohexanol selectivity was decreased from 97 % to 77 % in 1 h, and from 98 % to 86 % at the end of 4 h compared to Pt/C catalyst reduced at 600 °C (see Figures 5.7 and 5.8).

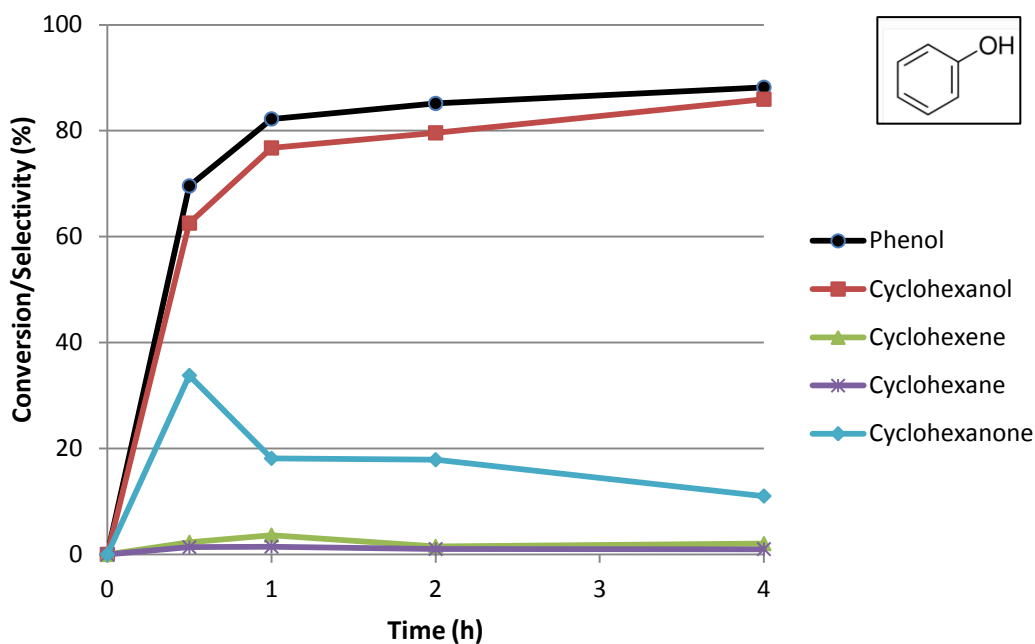


Figure 5.8 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Pt/C reduced at 800 °C.

It can be reported that increasing the mean Pt particle size from 3.10 nm to 3.69 nm did not cause an activity loss for phenol conversion. However, it caused a significant activity loss in cyclohexanol selectivity.

The different trends of Pt particle size effect on catalytic activity bring about a necessary trade-off in determining the optimal Pt particle size for catalyst in phenol hydrodeoxygenation. According to the present investigation, the mean particle size of around 2 nm is considered to be optimal for the activity of Pt/C catalyst in phenol hydrodeoxygenation.

5.2.5 Phenol hydrodeoxygenation in the presence of commercial Ru/C catalyst

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Ru/C catalyst in order to see phenol conversion and distribution of products obtained at the end of reactions. Figure 5.9 shows the conversion of phenol and selectivity of products occurred during the reactions versus reaction time.

In the presence of Ru/C catalyst, phenol conversion was achieved with high yields at the end of 4 h. As it is expected, cyclohexanol was again found as the dominant product, and cyclohexanone was detected as intermediate. Phenol conversion firstly reached to 44 % in 0.5 h, and after 2 h passed it was found as 100 %. Cyclohexanol

selectivity reached to 100 % within 1h, these findings are very similar to in which phenol was converted to cyclohexanol in the presence of commercial Pt/C catalyst (see Figure 5.4).

It is mentioned in the literature that it is also possible to obtain phenol conversion with high yields in the presence of ruthenium catalysts depending on the experimental conditions [47].

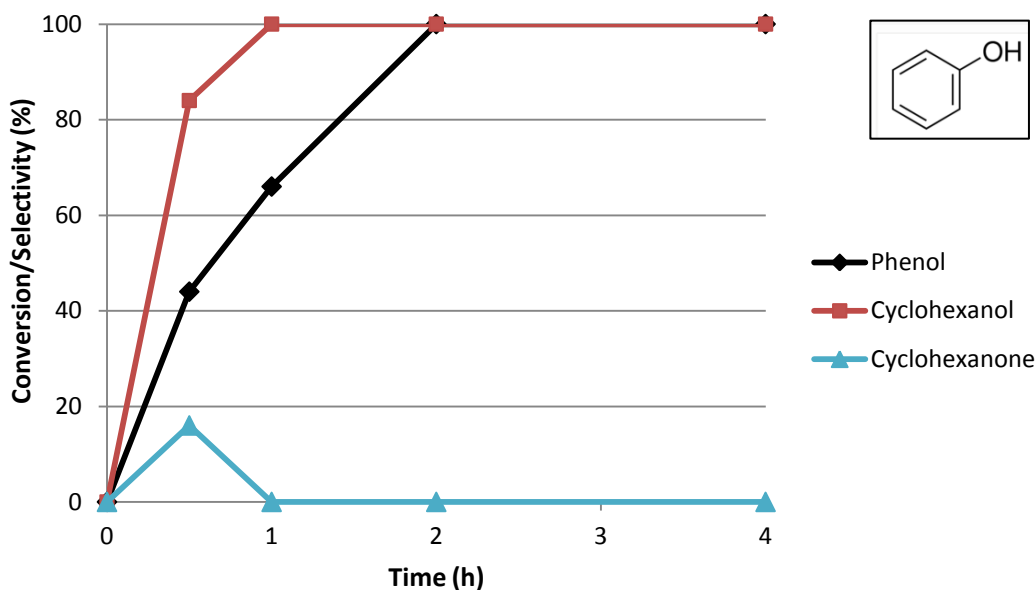


Figure 5.9 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Ru/C catalyst.

Furthermore, it is known from literature that besides Pt/C, other supported noble-metal catalysts such as Pd/C, Ru/C, Rh/C, Pd/Al₂O₃, and Pd/SiO₂ can efficiently convert phenol in neutral or acidic aqueous reaction medium to cycloalkanes [32].

5.2.6 Phenol hydrodeoxygenation in the presence of commercial Ru/Al₂O₃ catalyst

Phenol hydrodeoxygenation experiments were performed in the presence of commercial Ru/Al₂O₃ catalyst in order to see phenol conversion and distribution of products obtained at the end of reactions. Figure 5.10 shows the conversion of phenol and selectivity of products occurred during the reactions versus reaction time.

With respect to the experimental facts, in neutral water under conditions of 200 °C and 20 bar H₂, 84 % phenol conversion was achieved in 1 h, and it reached to 88 % in 4 h in the presence of Ru/Al₂O₃ catalyst. However, during the reactions

cyclohexanol did not reach to 100 % selectivity. As compared to commercial Ru/C and Pt/C catalysts under the same conditions, it can be reported that Ru/Al₂O₃ showed less catalytic activity for phenol conversion. Also, in this reaction, it can be seen from figure 5.10 that cyclohexanone was not totally consumed. Cyclohexanone selectivity reached to 37 % in 0.5 h, but after that it showed a decreasing tendency, and it was found as 9 % at the end of 4 h.

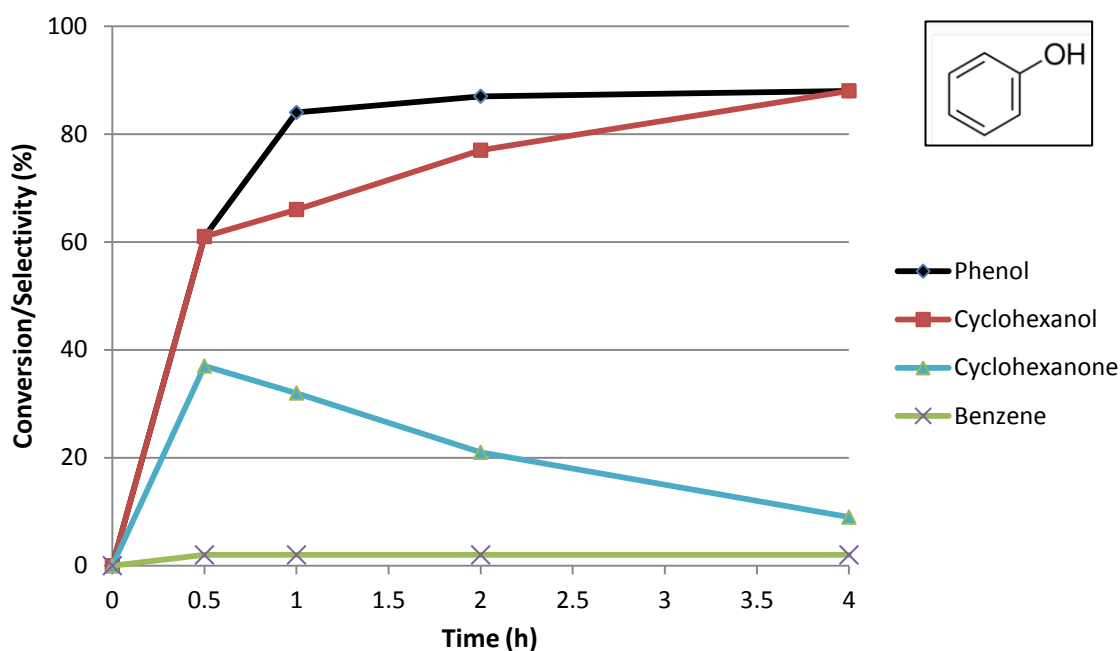


Figure 5.10 : Plot of phenol conversion and selectivity of monomeric products occurred during reaction in the presence of commercial Ru/Al₂O₃ catalyst.

On the other hand, it is already known that phenol conversion was achieved in the presence of commercial Ru/C catalyst in previous experiment. However, it is seen that selectivity of products is strongly related to support of the catalyst used. By the same token, Liu et al. observed that lewis acids such as AlCl₃, ZnCl₂, InCl₃, and SnCl₂ stabilized cyclohexanone intermediates in the presence of Pd/C [48]. Withal, Lercher et al. showed similar activities of Pd/C and Ru/C catalysts on phenol conversion in their research; therefore stabilized cyclohexanone selectivity and relatively less activity of Ru particles can be identified with presence of alumina support.

Another important thing to mention here is formation of benzene from phenol in the presence of Ru/Al₂O₃ catalyst. It can be seen from Figure 5.10 that benzene was

produced as the minor product in this reaction. Actually, this result is also reasonable, because it is known from literature that in the presence of hydrogenation catalysts, temperatures and pressures more than 200 °C and 10 bar, respectively, favour hydrogenolysis of phenol where C-OH bond is broken, and yield to benzene [49].

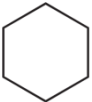
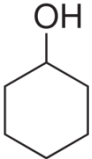
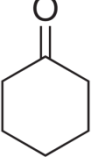
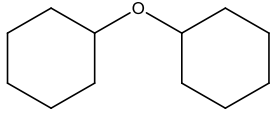
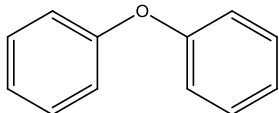
5.3 Hydrogenolysis of Dimeric Lignin Model Compounds

5.3.1 Hydrogenolysis of diphenyl ether

Hydrogenolysis experiments of diphenyl ether were carried out in the presence and absence of 0.5 wt. % phosphoric acid (H_3PO_4) by using commercial Pt/C catalyst in order to investigate the behavior of aryl–aryl ether bond and to see diphenyl ether conversion and distribution of products obtained at the end of reactions. To illustrate, chemical structures of diphenyl ether and reaction products are given in Table 5.2. Tables 5.3 and 5.4 show the conversion of diphenyl ether and products occurred during the reactions for normal and acidic cases, respectively.

Experimental findings show that in the presence of Pt/C catalyst and H_2 , diphenyl ether was fully converted after 0.5 h at 200 °C under non-acidic conditions (see table 5.3). During the reactions, cyclohexane, cyclohexanol and dicyclohexyl ether were detected as the main products. Regarding the product distribution, cyclohexane was found with the selectivity of 42 % after 0.5 h passed, and it showed increasing trend during the reaction. Final selectivity of it was calculated as 46 % at the end of 4 h. As to second abundant product cyclohexanol, it was detected with the selectivity of 29 % in 0.5 h, and it reached to 36 % at the end of 4 h. Concerning dicyclohexyl ether formation, it was observed with the highest selectivity of 18 % in 0.5 h at the beginning of the reaction. However, unlike cyclohexane and cyclohexanol, it did not show increasing trend, and its final selectivity was obtained at 11 % after 4 h passed. In the light of these findings, it can be reported that cyclohexane and cyclohexanol selectivity both showed linearly increasing change through the reactions while dicyclohexyl ether selectivity showed decreasing trend.

Table 5.2 : Chemical structures of compounds obtained in the oil from diphenyl ether hydrogenolysis experiments.

Compound	Chemical Formula	Nomenclatures	Structure
Cyclohexane	C_6H_{12}	A ₁	
Cyclohexanol	$C_6H_{12}O$	A ₂	
Cyclohexanone	$C_6H_{10}O$	A ₃	
Dicyclohexyl ether	$C_{12}H_{22}O$	A ₄	
Diphenyl ether	$C_{12}H_{10}O$	X	

Formation of cyclohexane and cyclohexanol can be explained by the fact that C-O bond cleavage was achieved under the reactions conditions. It can be remarked that ether bond is cleaved in a homolytic manner generates phenoxy radical and phenyl radical species, and these can recombine with hydrogen to form benzene and phenol. Then, in the presence of hydrogenation catalyst these components were fastly hydrogenated to form cyclohexane and cyclohexanol. However, on the other hand, dicyclohexyl ether formation shows that C-O bond cleavage of the reactant was not fully completed. Therefore, it can be speculated that ring hydrogenation and bond cleavage mechanisms begin at the same time (see Figure 5.11).

Phenol hydrodeoxygenation experiments show that cyclohexanol is formed from phenol in the presence of hydrogenation catalyst. Also, it can be concluded from previous experiments that cyclohexanone is appeared as an intermediate when the phenol is reactant. Hence, it can be claimed that cyclohexanol and cyclohexanone

were both formed via hydrogenation mechanism of phenol. On the other hand, it is clear that in order to obtain cyclohexane formation with high selectivity, acidic site must be present in the reaction medium. Consequently, the possible explanation for cyclohexane forming under non-acidic conditions is that it is originated from fast hydrogenation reaction of benzene. This result is in accordance with those reported by Choren et al. [50]. These authors pointed out that benzene is directly hydrogenated to cyclohexane in the presence of Pt particles in their research, but they also indicated that the activity of catalysts was significantly related to support used.

Table 5.3 : Conversion of diphenyl ether and selectivity of products in normal reaction medium.

Time (h)	X, %	Selectivity, %			
		A ₁	A ₂	A ₃	A ₄
0	0	0	0	0	0
0.5	100	42	29	11	18
1	100	43	31	6	19
2	100	45	34	9	12
4	100	46	36	6	11

In the presence of acidic site, 100 % conversion of diphenyl ether was obtained as cyclohexane was calculated with the selectivity of 54 % in 0.5 h, and final cyclohexane selectivity was obtained as 97 % at the end of 4h. Compared to non-acidic conditions, cyclohexane selectivity is found as 2 times more under acidic conditions. Moreover, it can be seen from Table 5.4 that cyclohexanol was totally consumed after 4 h passed, whereas it showed linearly increasing trend in normal reaction medium.

Table 5.4 : Conversion of diphenyl ether and selectivity of products in acidic reaction medium.

Time (h)	X, %	Selectivity, %			
		A ₁	A ₂	A ₃	A ₄
0	0	0	0	0	0
0.5	100	54	27	3	17
1	100	73	14	2	11
2	100	81	7	2	10
4	100	97	0	0	3

This result is expected since the hydronium ion coming from phosphoric acid reacts with hydroxyl group connected to cyclic monomer, and this lead cyclohexanol to be converted to cyclohexane as well. Cyclohexanone is again found as an intermediate product originated from phenol hydrodeoxygenation as it is expected.

Another important issue to mention is though full hydrogenation of the reactant is achieved for both cases, uncompleted depolymerization of diphenyl ether was observed along with the reactions. However, the selectivity of dicyclohexyl ether showed decreasing trend, and therefore it can be said that full depolymerization of the reactant requires longer reaction times than 4 h. Figure 5.11 summarizes the overall reaction mechanism of diphenyl ether.

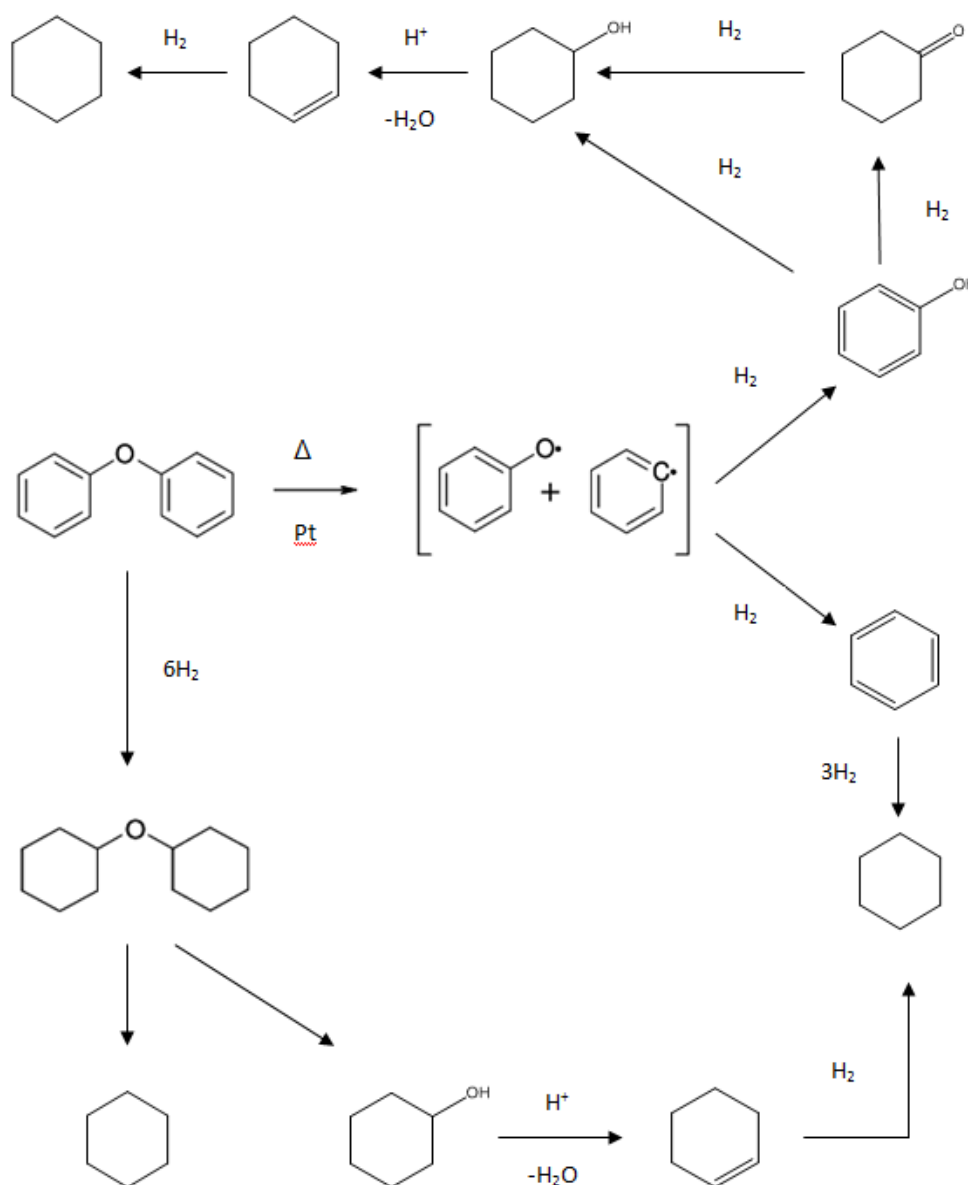

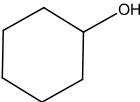
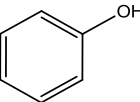
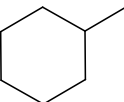
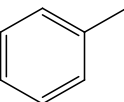
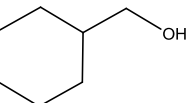
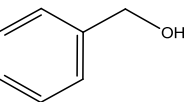
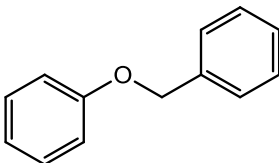


Figure 5.11 : Possible reaction mechanism of diphenyl ether to monocyclics.

5.3.2 Hydrogenolysis of benzyl phenyl ether

Hydrogenolysis experiments of benzyl phenyl ether were performed in the presence and absence of 0.5 wt. % phosphoric acid (H_3PO_4) by using commercial Pt/C catalyst in order to investigate the behavior of alkyl–aryl ether bond and to see benzyl phenyl ether conversion and distribution of products obtained at the end of reactions. Chemical structures of benzyl phenyl ether and monomeric reaction products are given in Table 5.5, and dimeric reaction products are given in Table 5.6. Tables 5.7 and 5.8 show the conversion of benzyl phenyl ether and products occurred during the reactions versus reaction time for normal and acidic cases, respectively.

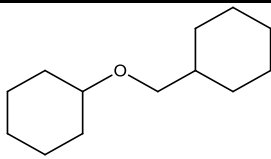
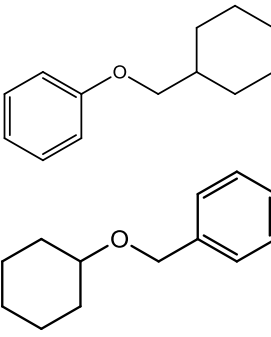
Table 5.5 : Chemical structures of benzyl phenyl ether and monomeric compounds obtained in the oil from benzyl phenyl ether hydrogenolysis experiments.

Compound	Chemical Formula	Nomenclatures	Structure
Cyclohexane	C_6H_{12}	B ₁	
Cyclohexanol	$\text{C}_6\text{H}_{12}\text{O}$	B ₂	
Phenol	$\text{C}_6\text{H}_6\text{O}$	B ₃	
Methylcyclohexane	C_7H_{14}	B ₄	
Toluene	C_7H_8	B ₅	
Cyclohexanemethanol	$\text{C}_7\text{H}_{14}\text{O}$	B ₆	
Benzyl alcohol	$\text{C}_7\text{H}_8\text{O}$	B ₇	
Benzyl phenyl ether	$\text{C}_7\text{H}_{12}\text{O}$	X	

Experimental findings show that in the presence of Pt/C catalyst and H₂, benzyl phenyl ether was fully converted in 2h at 200 °C. It can be seen from Table 5.7 that cyclohexanol, phenol, methylcyclo hexane and toluene were found as the most abundant monomeric compounds under non-acidic reaction conditions. Selectivity of phenol was calculated as 21 % within 0.5 h, and then it showed a decreasing trend through the reaction, and was finally consumed in 4 h. On the contrary, cyclohexanol selectivity firstly reached to 10 % in 0.5 h, and after that was increased with prolonged reaction time up to 29 %.

Likewise, toluene was found as the most abundant monomer among the reaction products occurred in 0.5 h with the selectivity of 30 %. However, its selectivity was getting decreased with increasing reaction time, and it was found as 20 % at the end of 4h while selectivity of methylcyclo hexane was getting increased (see Table 5.7). On the other hand, traces of benzyl alcohol and cyclohexanemethanol were found in reaction medium as well. Apart from monomerics, saturated dimerics, semi-saturated dimerics and recombination products were also detected during the reactions.

Table 5.6 : Chemical structures of dimeric compounds obtained in the oil from benzyl phenyl ether hydrogenolysis experiments.

Compound	Chemical Formula	Nomenclatures	Structure
Saturated dimer	C ₇ H ₁₈ O	B ₈	
Semi-saturated dimers	C ₇ H ₁₅ O	B ₉	

Formation of toluene and phenol monomers implies that ether bond was cleaved homolytically as in a pyrolysis reaction, in which phenoxy and benzyl radicals are generated, and in the presence of high pressure H₂, being highly reactive, they

reacted with it to produce phenol and toluene. As it was observed in phenol hydrodeoxygenation reactions and known also from literature that cyclohexanol formation is originated from phenol in the presence of hydrogenation catalyst. Comparably, methylcyclo hexane formation can be ascribed to presence of toluene in reaction medium. As it can be seen from Table 5.7 that methylcyclo hexane selectivity was increased while toluene selectivity was decreased.

As to formation of benzyl alcohol during reaction, Yokoyama et al. [51] suggest that heterolytic cleavage of ether bond is responsible for benzyl alcohol and phenol generation (see Figure 5.12). Thus, it can be claimed that cyclohexanemethanol is formed via hydrogenation reaction of benzyl alcohol in the presence of Pt/C catalyst.

Furthermore, as it can be seen from Table 5.7 that partial hydrogenation of benzyl phenyl ether shows decreasing trend through the reaction. The possible explanation for these circumstances is bond cleavage and ring hydrogenation begins at the same time, and therefore semi-saturated dimeric compounds are appeared as intermediates. In the latter case, formation of recombination products can be attributed to monomers occurred. These monomers may recombine among themselves and/or react with benzyl phenyl ether or its derivatives.

Table 5.7 : Conversion of benzyl phenyl ether and selectivity of products in normal reaction medium.

Time (h)	X, %	Selectivity, %									Recombination products
		B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉	
0	0	0	0	0	0	0	0	0	0	0	0
0.5	81	0	10	21	10	30	2	0	8	19	10
1	95	0	12	18	11	29	0	0	11	13	6
2	100	0	20	16	14	25	2	3	13	0	7
4	100	0	29	0	25	20	0	5	11	0	10

In the presence of phosphoric acid, and under the same conditions, benzyl phenyl ether conversion was found as 92 % within 2 h, and it reached to 100 % in 4 h. In this case, instead of cyclohexanol, cyclohexane became one of the most dominant reaction products. Selectivity of it was found as 9 % in 0.5 h, and proceeded with increasing tendency. It was calculated as 20 % at the end of 4 h while cyclohexanol was being consumed totally after 4 h passed. Additionally, phenol and toluene were again found with relatively high yields as it is expected.

In these reactions, as acidic site introduced to the reaction medium, and it is known from hydrodeoxygenation reaction of phenol, therefore it can be remarked that cyclohexane was formed via hydrogenation reaction of cyclohexanol (see Figure 5.5). Even though the selectivity of methylcyclohexane did not linearly change with increasing reaction time, it is known that it is formed via hydrogenation reaction of toluene in the presence of hydrogenation catalyst. By the same token, it can be said that cyclohexane methanol was also formed from benzyl alcohol as it is expected.

Saturated and semi-saturated forms of benzyl phenyl ether were detected. However, semi-saturated form of it was again found as an intermediate. This means that full hydrogenation of benzyl phenyl ether was completed at the end of the 4 h. On the other hand, especially in the acidic case of benzyl phenyl ether reactions, nonlinear selectivity change of monocyclics were observed (see Table 5.8), this can be associated with the formation and decomposition of trimers and/or dimeric recombination products along with the reactions. Another reason for these circumstances can be lack of extraction step where organic phase is separated from aqueous phase.

Table 5.8 : Conversion of benzyl phenyl ether and selectivity of products in acidic reaction medium.

Time (h)	X, %	Selectivity, %									Recombination products
		B ₁	B ₂	B ₃	B ₄	B ₅	B ₆	B ₇	B ₈	B ₉	
0	0	0	0	0	0	0	0	0	0	0	0
0.5	64	9	6	18	12	23	0	6	7	10	9
1	78	6	5	26	5	18	0	14	7	8	11
2	92	18	4	23	0	23	0	12	5	5	10
4	100	20	0	23	13	28	3	0	4	0	9

5.3.3 Hydrogenolysis of biphenyl

Hydrogenolysis experiments of biphenyl were performed in the presence and absence of 0.5 wt. % phosphoric acid (H₃PO₄) by using commercial Pt/C catalyst in order to see biphenyl conversion and distribution of products obtained at the end of reactions. Figures 5.13 and 5.14 plot the yield of biphenyl and product occurred during the reactions versus reaction time for normal and acidic cases, respectively.

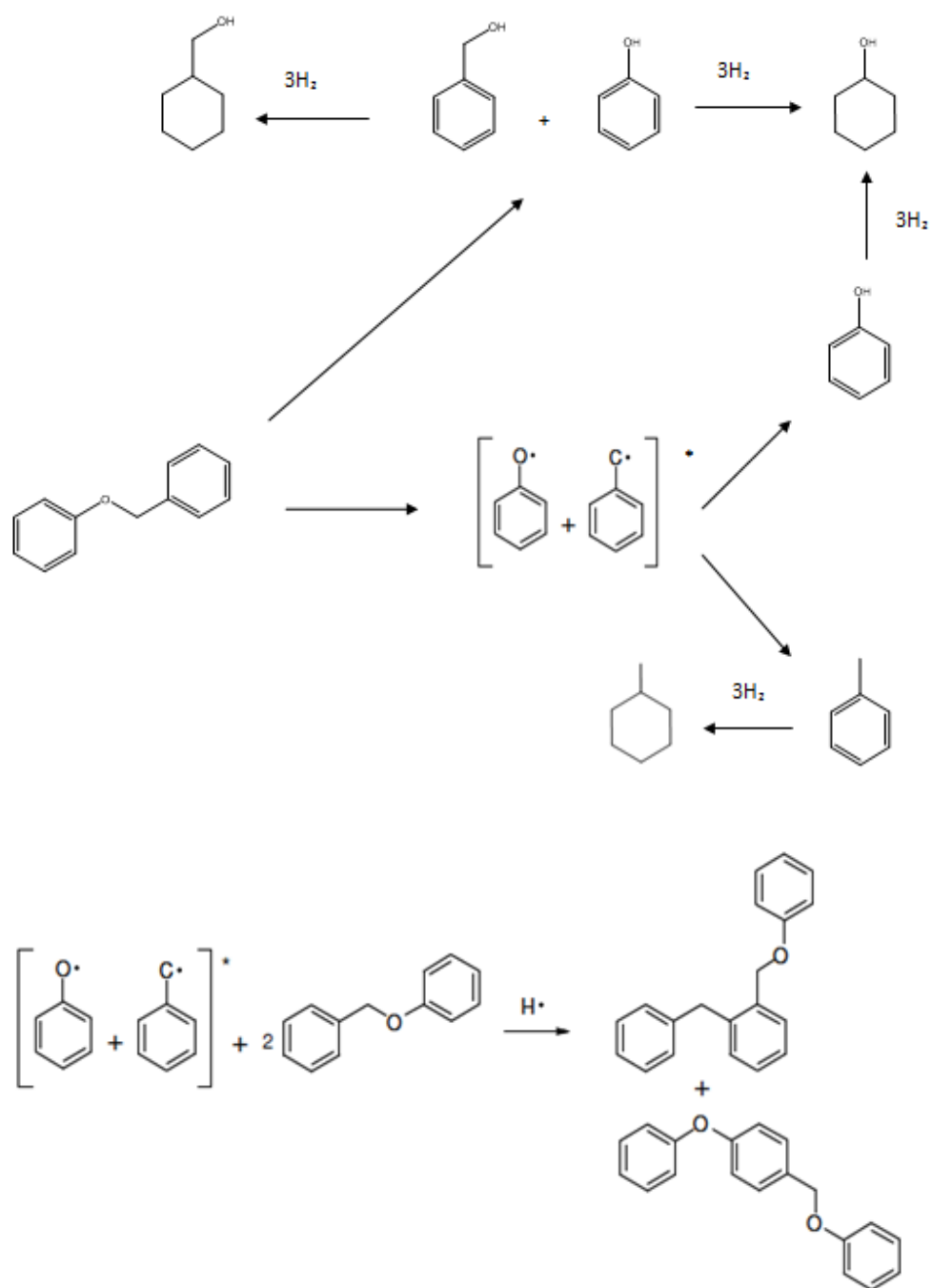


Figure 5.12 : Possible reaction mechanism of benzyl phenyl ether to monocyclics and recombination products.

According to the GC/MS and GC/FID findings, bicyclohexyl was detected as the single dominant dimeric product obtained at the end of the hydrogenolysis reactions of biphenyl. This result implies that C-C bond cleavage between two aromatic rings was not achieved in both neutral and acidic reaction mediums under conditions of 200 °C and 20 bar H_2 . On the other hand, however, it can be said that hydrogenation of aromatic rings was achieved under the same conditions, and 100 % biphenyl

conversion was observed in 0.5 h in both neutral and acidic cases (see Figures 5.13 and 5.14).

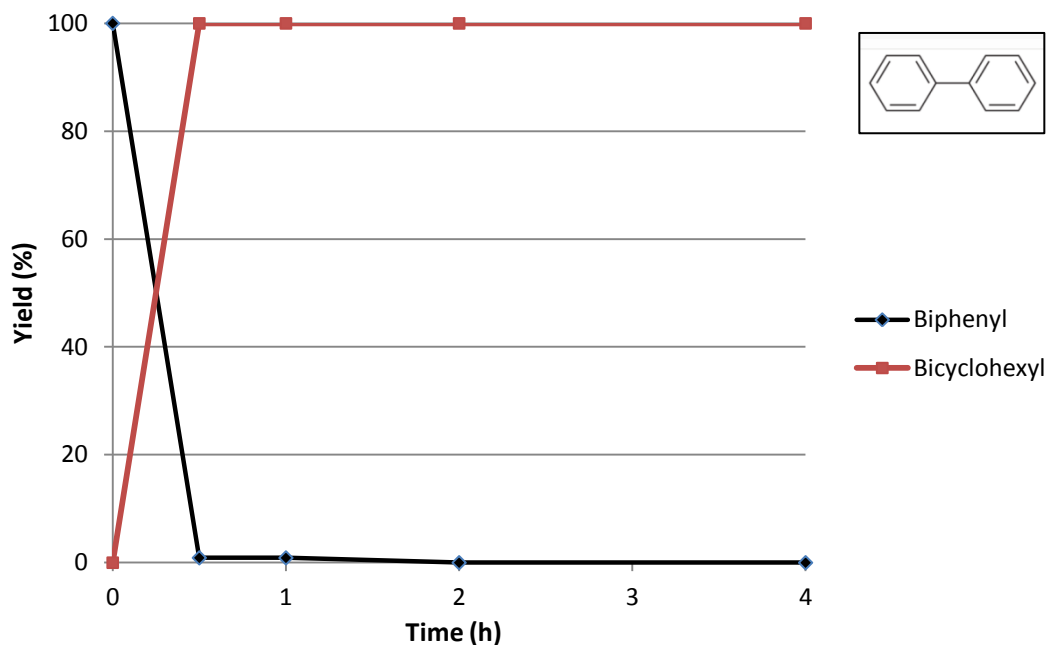


Figure 5.13 : Plot of biphenyl and bicyclohexyl yield during reaction in the presence of commercial Pt/C catalyst in neutral reaction medium.

Moreover, increasing the acidity of reaction medium did not result in a change on the product distribution. The representative chemical structures of biphenyl and bicyclohexyl are shown in Figure 5.15.

As it is mentioned previously in the literature that the cleavage of C-C bonds needs more severe conditions [5, 11, 19], and therefore monomeric products are not expected from biphenyl at the temperature around 200 °C. Besides, it is already known that noble catalysts such as Pt/C and Pd/C are able to hydrogenate the aromatic rings of the reactants in aqueous phase at the temperatures between 200 and 300 °C [44]. In the light of these findings, it can be reported that biphenyl can be easily hydrogenated to bicyclohexyl in the presence of Pt/C catalyst under conditions of 200 °C and 20 bar H₂.

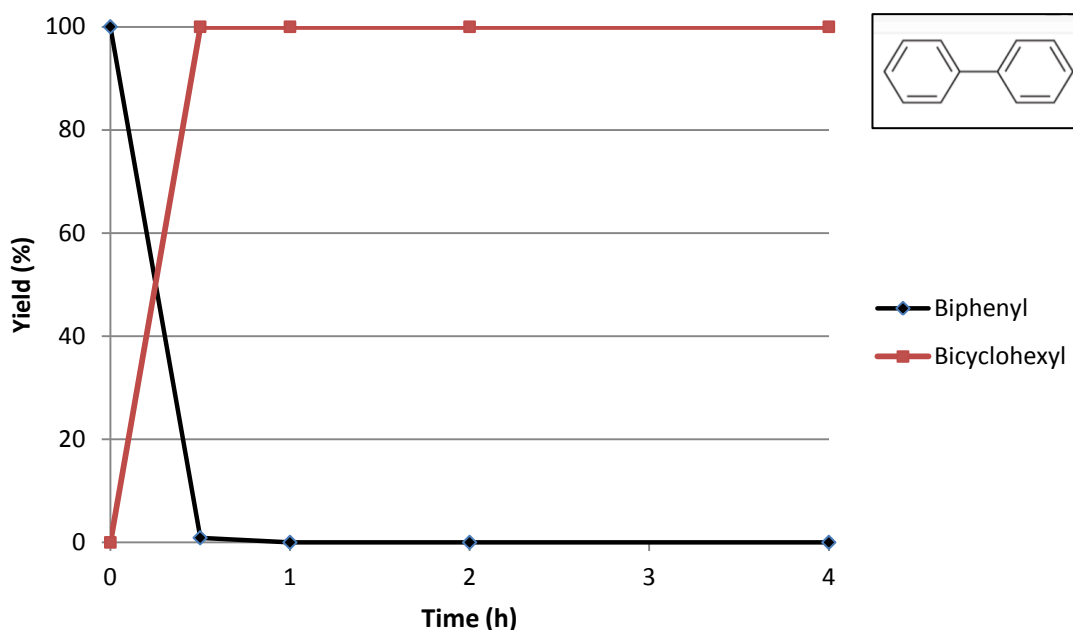


Figure 5.14 : Plot of biphenyl and bicyclohexyl yield during reaction in the presence of commercial Pt/C catalyst in acidic reaction medium.

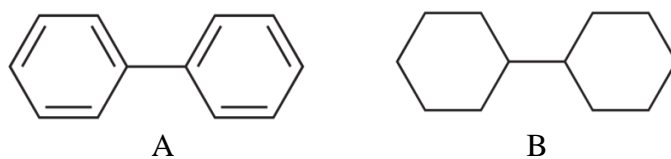


Figure 5.15 : Chemical structures of biphenyl (A) and bicyclohexyl (B).

5.3.4 Hydrogenolysis of diphenyl methane

Hydrogenolysis experiments of diphenyl methane were performed in the presence and absence of 0.5 wt. % phosphoric acid (H_3PO_4) by using commercial Pt/C catalyst in order to see diphenyl methane conversion and distribution of products obtained at the end of reactions. Figures 5.16 and 5.17 plot the yield of diphenyl methane and products obtained during the reactions versus reaction time for normal and acidic cases, respectively.

Experimental findings show that 100 % diphenyl methane conversion was achieved in 0.5 h under conditions of 200 °C and 20 bar H_2 in the presence of commercial Pt/C catalyst (see Figures 5.16 and 5.17) both for neutral and acidic cases. However, as to products occurred during the reactions, mainly two different dimeric compounds were detected by GC/MS instrument. One of these products is dicyclohexyl methane, and the other one is benzyl cyclohexane.

It is clearly known that Pt/C catalyst is able to hydrogenate the aromatic ring under conditions of 200 °C and 20 bar H₂. It can be seen from Figures 5.16 and 5.17 that dicyclohexyl methane is found as the most abundant product, and its selectivity was getting higher while benzylcyclo hexane selectivity was getting lower through the reaction. The possible explanation for this circumstance is that diphenyl methane was not only hydrogenated to dicyclohexyl methane, but also hydrogenated to benzylcyclo hexane at the same time in the first step. In the second step, benzylcyclo hexane was hydrogenated to dicyclohexyl methane as well, and therefore benzylcyclo hexane appeared as an intermediate during the reaction (see figure 5.18). On the other hand, there was not any monomeric compound detected along with the reactions, and this implies that C-C bond cleavage was not achieved under the reaction conditions. This result is in accordance with biphenyl results, under the same conditions C-C bond cleavage was also not achieved when biphenyl was the reactant.

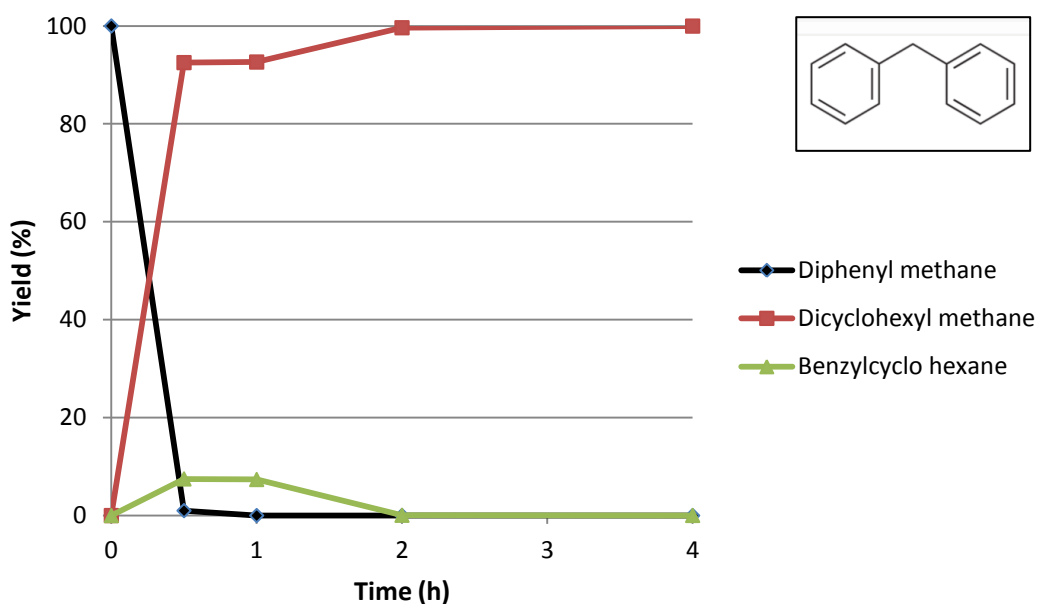


Figure 5.16 : Plot of diphenyl methane and products yield during reaction in the presence of commercial Pt/C catalyst and normal reaction medium.

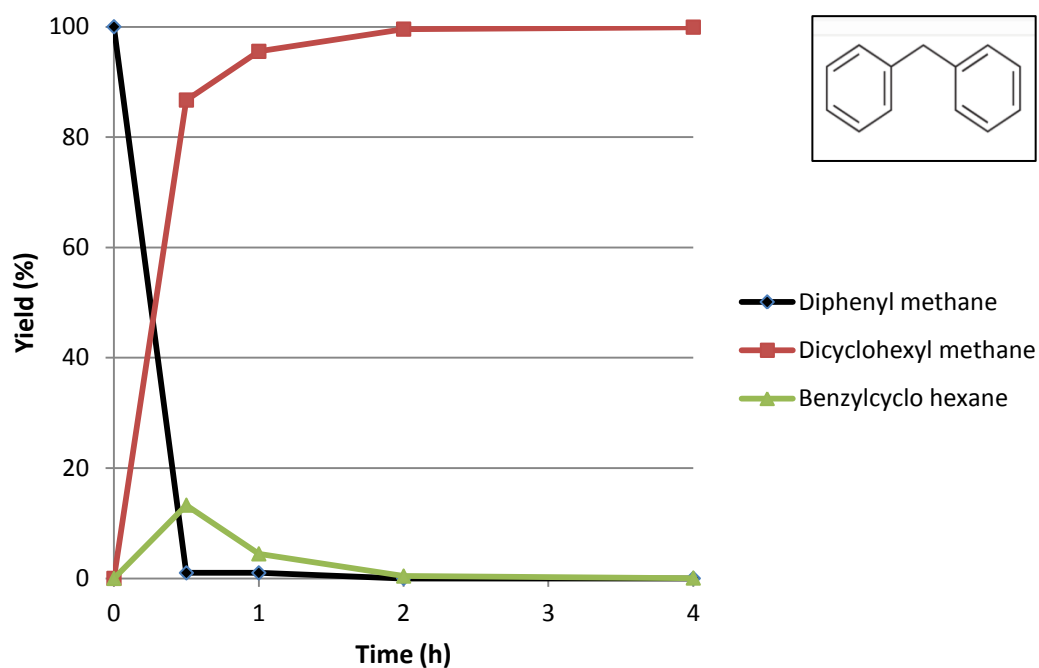


Figure 5.17 : Plot of diphenyl methane and products yield during reaction in the presence of commercial Pt/C catalyst and acidic reaction medium.

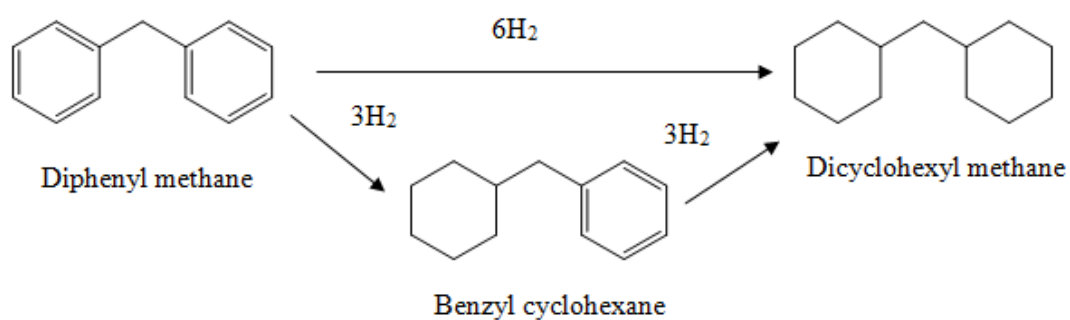


Figure 5.18 : Reaction pathways of diphenyl methane to benzyl cyclohexane and dicyclohexyl methane in the catalytic hydrogenation treatment.

6. CONCLUSIONS AND RECOMMENDATIONS

The aim of this study was to probe the possibility of deriving alternative fuel components from lignin by using monomeric and dimeric model compounds of it as reactants. The results of the research show that model compounds such as phenol, diphenyl ether, benzyl phenyl ether, diphenyl methane and biphenyl can be converted into monomeric and/or dimeric units under the applied conditions depending on the chemical structure of the reactant. First of all, it is possible to enhance the conversion ratio by increasing the reaction time.

Experimental findings of phenol showed that untreated commercial Pt/C catalyst yielded significantly to cyclohexanol while phenol conversion was achieved nearly 100 % under conditions of 200 °C and 20 bar. However, when 0.5 wt. % H₃PO₄ introduced to the reaction medium, cyclohexane was observed as the most abundant product along with the reaction. Considering ruthenium particles on different supports such as activated carbon and alumina, it can be indicated that phenol conversion was achieved with high yields, but presence of alumina support made cyclohexanone more stable in reaction medium with the selectivity of 38 % in 0.5 h. Besides, a trace of benzene was observed in this reaction, and it can be attributed to hydrogenolysis of phenol under applied conditions. Considering Pt particle size effect on catalytic activity for phenol conversion, increasing the mean particle size from 2.03 nm to 3.10 nm caused an activity loss from 100 % to 86 % at the end of 4 h. On the other hand, increasing it from 3.10 nm to 3.69 nm did not result in activity loss at all. The activity loss of Pt particles can be ascribed to the decreased active surface area of Pt particles.

In the case of dimeric model compounds, it can be concluded that final product distribution significantly depends on the chemical structure of the model compound. Under the applied conditions, C-C bond cleavage was not achieved in both neutral and acidic conditions, and thus monomeric units were not detected when the biphenyl and diphenyl methane were the reactants. However, 100 % conversion and hydrogenation of these compounds were achieved in the presence of commercial

Pt/C catalyst in 0.5 h. As the largest fraction of bonds in lignin is of the aryl-alkyl ether type, benzyl phenyl ether investigation gives us the most valuable results. In both neutral and acidic reaction mediums, the conversion of benzyl phenyl ether reached to 100 % at the end of 4 h, and phenol and toluene were observed as the most abundant monomeric units. In addition to this, reasonable amount of cyclohexanol, with increasing trend was also identified. Benzyl alcohol was also found in reaction medium. These monomeric units implies that C-O bond of benzyl phenyl ether was cleaved in the presence of commercial Pt/C catalyst under conditions of 200 °C and 20 bar H₂. Concerning aryl-aryl bond in diphenyl ether, it was broken down in homolytic manner yielding to benzene and phenol which were then hydrogenated to cyclohexane and cyclohexanol. Other than monomerics obtained, semi-saturated and saturated forms of compounds were observed either in benzyl phenyl ether and diphenyl ether experiments. This implies that bond cleavage and ring hydrogenation begin at the same time.

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CURRICULUM VITAE



Name Surname: Osman KURŞUN

Place and Date of Birth: Bergama,11.03.1985

Address: Üsküdar-ISTANBUL

E-Mail: osmankursun@itu.edu.tr

B.Sc.: Anadolu University, Chemical Engineering

M.Sc. : Istanbul Tehnical University, Chemical Engineering