EFFECT OF ZEOLITE ON THE CATALYTIC CRACKING OF TAR YIELDS MAHOGANY WOOD PYROLYSIS

Widya Wijayanti

Brawijaya University,
Mechanical Engineering
Departement, Malang,
Indonesia

Mega Nur Sasongko

Brawijaya University,
Mechanical Engineering
Departement, Malang,
Indonesia

Musyaroh

Brawijaya University,
Mechanical Engineering
Departement, Malang,
Indonesia

Cite article:

Wijayanti W., Sasongko Nur M., Musyaroh (2021) EFFECT OF ZEOLITE ON THE CATALYTIC CRACKING OF TAR YIELDS MAHOGANY WOOD PYROLYSIS, *Journal of Applied Engineering Science*, 19(4), 989 - 995, DOI:10.5937/ jaes0-29995

Online aceess of full paper is available at: www.engineeringscience.rs/browse-issues

EFFECT OF ZEOLITE ON THE CATALYTIC CRACKING OF TAR YIELDS MAHOGANY WOOD PYROLYSIS

Widya Wijayanti*, Mega Nur Sasongko, Musyaroh
Brawijaya University, Mechanical Engineering Departement, Malang, Indonesia

In this study, the effects of zeolite were observed to investigate the formation of a pyrolysis product, which is tar yield. Tar yields receive the most attention because of their potential as a bio-oil and chemical feedstocks. For this reason, efforts to increase tar yield were made, one of which was by adding zeolite to the pyrolysis process. The role of zeolite here was a pyrolysis catalyst. This is a study that uses mahogany wood as the feedstock for a real, pilot plant pyrolysis reactor. Moreover, 0–50% of the feedstock's mass worth of zeolite was also introduced during the pyrolytic process. The temperatures set in this pyrolysis were 250 °C, 500 °C, and 800 °C. The test results were measured in terms of the tar yield's volume and mass. The volume of tar yields produced increased as the temperature increased due to more biomass decomposed. Then, the chemical composition of tar yield was tested using a Gas Chromatograph Mass Spectrometry (GC-MS) to measure the percentage of its chemical constituent compounds. Then, the formation mechanism of tar compounds from pyrolysis was described by using HyperChem simulation. The results showed that an increase in zeolite catalyst percentage would generate more volume of tar yields. It was due to the breaking of biomass hydrocarbon chains, increasing the production of tar yields. Zeolite also affected the formation of hydrocarbon chains in tar yields where the chains became shorter as the percentage of zeolite catalyst rose. The mechanism of increasing tar product was due to the role of zeolite as a catalyst in the catalytic cracking process which is almost similar to acid-base reactions of Brønsted-Lowry and Lewis. This reaction took place when the pyrolysis yields moved through the pores of zeolite, breaking the long hydrocarbon chains into shorter ones which were dominated by alkenes, aromatic, and acidic compounds formation. In addition, acidic compounds represented by acetic acid function as a flammable matter possess the potential of becoming oil-fuel.

Key words: zeolite, catalytic cracking, tar, mahogany wood, pyrolysis

INTRODUCTION

Pyrolysis is a method for converting biomass into fuel, whether as a solid, gas, or liquid fuel. Various attempts have been made to increase pyrolysis production. During pyrolysis, complex hydrocarbon molecules in biomass break down into relatively smaller and simpler gas, liquid, and carbon [1]. In principle, pyrolysis is the breakdown of biomass into shorter compounds due to the complexity (length) of the biomass compounds. Therefore, other process is needed to break these long hydrocarbon compounds into simpler ones. There are two methods to decompose these complex biomass compounds: thermal cracking and catalytic cracking process. There has been plenty of research on thermal cracking, but research on catalytic cracking has not yet been done. In this study, both methods were used, though the catalytic cracking effect was focused more. Catalytic cracking is the process of breaking the chain of hydrocarbons into short-chained hydrocarbons with the help of a catalyst [2].

An appropriate matter used as the catalyst is zeolite. Zeolite is commonly used as a catalyst and adsorbent. Previous research [3] to [4] described that zeolite as a microporous structure is capable of absorbing H+ ion decomposed at the major compound. In thermal cracking, the condensed gas will be decomposed by introducing heat energy absorbed during the process to crack longer hydrocarbon compounds into shorter ones. If catalytic cracking is involved in the process, not only is the pyrolysis process influenced by heat, but the catalyst will also absorb and dissociate the compounds which pass through the zeolite pores and then split into shorter-chain compounds. There are many studies [5] to [8] investigating the effects of zeolite. However, an explanation of the mechanism of tar yield formation has not been carried out. When the temperature starts to increase, the biomass undergoes thermal cracking where its structure is split from solid into condensed gas. The biomass compound decomposition is then met with the catalyst, zeolite, which holds a crucial role during this stage.

The process of breaking biomass chains by catalytic cracking process involves the acid-base process of Brønsted-Lowry and Lewis in zeolites [9]. Zeolite, a porous aluminosilicate mineral that carries a negative charge, is made of a tetrahedral structure of alumina (AlO_4) and silica (SiO_4). Zeolites act as cation exchangers, due to the negative nature of aluminum and the ability to exchange cations with compounds that pass through them. Zeolites are relatively cheap and easy to find. The content of AlO_4 and SiO_4 which form the tetrahedral structure of zeolites has two sources of acidity, namely the Brønsted-Lowry and the Lewis acid site [10]. The negative charge of aluminum in the zeolite's tetrahedral structure requires cations to balance it. This is because aluminum

substitutes silicon, making it a Brønsted-Lowry acid site. Therefore, Al will bind with H^+ ions and form a strong Brønsted-Lowry acid so that one part of the zeolite structure will bind to the H^+ ion as shown in Figure 1.
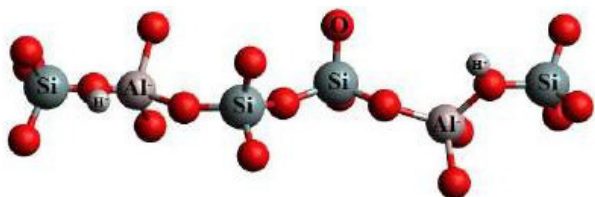

Figure 1: Brønsted-Lowry Acid Site at zeolite structure
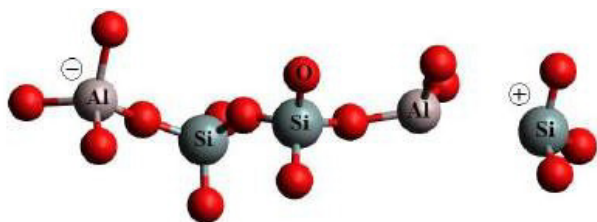

Figure 2: Lewis Acid Site at zeolite structure

Lewis Acid Site as the catalytic process in breaking the biomass is formed from extra-framework Aluminum in the zeolite structure. The term "extra-framework" refers to the aluminum in zeolite compounds, despite not forming a tetrahedral structure. Lewis acid site only acts as an acceptor or negative ion acceptor as determined in Figure 2. Both Brønsted-Lowry and Lewis acid-base reactions take place when the pyrolysis gas moves through the zeolite pores and breaks the long hydrocarbon chains into short ones [11].

This study takes into account the biomass compounds' breaking process, which will help illuminate the mechanism of the chemical tar yield formation. It will predict the effect of adding zeolite as a catalyst, proven by any chemical tar yields' compounds measurements. During the catalytic pyrolysis, zeolite was mixed with the mahogany feedstock in the pyrolysis reactor to study its effect and chemical mechanism formations on the final product yields.

EXPERIMENTAL METHODS

Pyrolysis was carried out on a fixed bed reactor as shown in Figure 3. In this experimental study, a heater was used to heat the furnace from Ts=250 °C to 800 °C. The feedstock used in the pyrolysis process came from any craft waste; needle particles of mahogany wood. To reduce their moisture level to around 0-2%, the feedstocks were subjected to a temperature of 110 °C in an oven for an hour prior to the experiment. Besides, it was used zeolite mixed with mahogany wood to investigate the effect of catalytic cracking in the pyrolysis process. The zeolite was obtained from South of Malang, Indonesia which contains elemental composition of natural zeolite minerals determined in Table 1.

Table 1: Elemental compositions of zeolite

Element	Weight %	Weight % σ	Atomic %
Carbon	31.833	4.511	41.578
Oxygen	48.875	3.319	47.926
Aluminum	3.481	0.299	2.024
Silicon	13.557	0.963	7.573
Potassium	1.724	0.198	0.692
Calcium	0.529	0.135	0.207

Simultaneously, the zeolite was activated and dried using a heating oven at a temperature of 400°C for one hour. This was also to ensure that the moisture content also reaches 0-2%, similar to the moisture content of mahogany, to initiate the pyrolysis process to suppress the moisture. The next step was to introduce 0-50% of the feedstock's mass worth of zeolite into the mahogany wood in the form of sawdust. Each mixture was ensured to weigh 200 grams.

Then, the feedstock mixture was put into the furnace reactor. After placing the feedstock, nitrogen gas was flowed inside the furnace to suppress oxygen for preventing combustion. Afterwards, the experiment was initiated with a designated heating rate of up to about 1073 K/h. After each experiment was completed, the tar
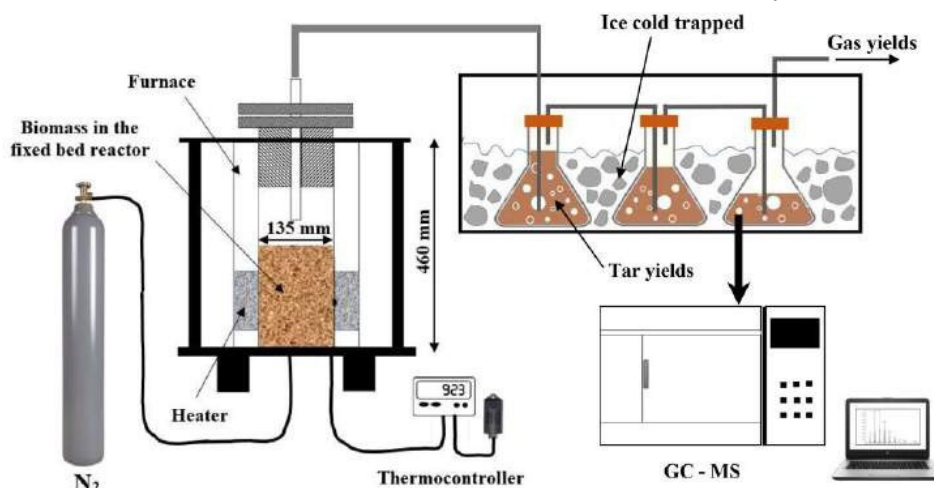

Figure 3: Experimental apparatus for obtaining tar yields of pyrolysis

yields of pyrolysis products were condensed in the beaker glass inside an ice-cold trap. Afterwards, at each pyrolytic setting temperature Ts, the volume of tar yield was measured using a flowmeter.

In addition to measuring the tar volume, the constituent chemical compounds of tar yield as the product of pyrolysis were also analyzed using GC-MS for investigating the effect of zeolite on the formation mechanism of tar's constituent compounds. Moreover, HyperChem simulation was used to validate the way by which zeolite plays a role in the formation of tar.

RESULTS AND DISCUSSION

The effects of zeolite on the production of tar yields

In this study, it was found that the effect of thermal cracking and catalytic cracking was indicated by the relationship between pyrolysis temperature and tar volume yield produced by the pyrolysis of mahogany wood at temperatures of 250 °C, 500 °C, and 800 °C. Moreover, this study also takes catalytic cracking affected by zeolite into account by adding zeolite at a percentage of 0%, 25%, and 50% as shown in Figure 2. First, in the absence of zeolite, the result suggests that temperature determines the volume of tar produced during the pyrolysis process [12]. The least volume of tar is produced at T=250°C because only softer compounds decompose at such low temperatures, such as cellulose and hemicellulose. On the contrary, a much higher temperature is needed to decompose harder compounds, which is lignin. At 500°C, there is an increase in the volume of tar yields (60 ml) by pyrolysis without zeolite. The reason for this increase is that hemicellulose begins to decompose at temperatures from 220–315°C, while cellulose at temperatures from 315–400°C [13].

The volume of tar yields produced increases as the temperature increases due to more biomass decomposing. When the pyrolysis temperature reaches above 500°C without the addition of zeolite, the volume of tar yields decreases because the primary tar begins to break down and forms secondary tar up to a temperature of 800°C when the primary tar has been finally used up [14].

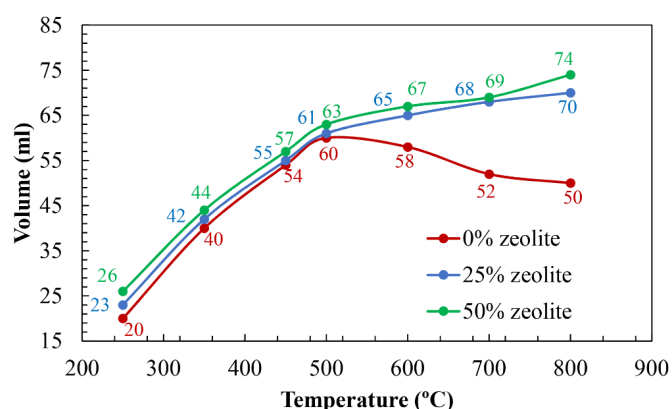Afterward, if we take a look at the effect of adding zeolite,

it shows that the produced tar yields with the addition of zeolite tend to be higher in terms of volume than without zeolite. This study found that the highest tar volume is in pyrolysis with 50% zeolite, followed by the addition of 25% zeolite and 0% zeolite. In this process, zeolite contributes to a significant amount of obtained pyrolysis process yields. This is because in pyrolysis without zeolite, the biomass is only decomposed through the thermal cracking process, i.e. the breakdown of chemical structures due to heat energy. Meanwhile, by adding zeolite, two decomposition processes take place at once; thermal cracking and catalytic cracking. Zeolite, as a catalyst, contributes to the decomposition of hydrocarbon chains through a catalytic cracking mechanism. If comparisons are made among them, the absence of zeolite leads to the pyrolysis occurring solely by the thermal cracking process.

Beyond the pyrolysis temperature of 500°C, there is a decrease in the volume of produced tar yields in the absence of zeolite, whereas increased tar yields happen with the addition of zeolite. This is because zeolite optimizes secondary and tertiary pyrolysis processes by absorbing H^+ ions in temperatures above 500 °C through the catalytic cracking method because zeolites are heat-resistant up to 1000°C [15]. Secondary pyrolysis reaction occurs above 500°C and produces secondary pyrolysis products, such as phenols and C_nH_{2n} alkene compounds as confirmed in section 3.2 below. Meanwhile, the addition of 25% and 50% zeolite indicates that the trend continues to increase. The addition of zeolites will continue to increase the yields because zeolites also have the ability to reduce the activation energy needed by biomass to be decomposed. In other words, compounds with stronger molecular bonds, such as hemicellulose and lignin can then be decomposed much easier.

The effects of zeolite on the constituent compounds of tar yields

This study used the GC-MS measurement to shed light on the influence of zeolite on the underlying mechanism of how tar yields are formed. Aside from explaining the mechanism of tar yield formation using HyperChem simulation validations, the identification aims to determine the distribution of tar yields' chemical composition that can be used as a liquid fuel (bio-fuel). In this study, we measured the tar yields by GC-MS, all in pyrolysis temperatures of 250°C–800°C. However, it is determined that T=500°C represents all of the GC-MS results as shown in Table 2 to Table 4.

In the tables, different hydrocarbon chain molecules can be seen where they can be classified based on chain length. The length of carbon chains in hydrocarbons are grouped into short, medium, and long carbon chains. The short carbon chain is in the C_1-C_3 range, medium chain in the C_4-C_6, while long chain in the C_7-C_{20} range [16]. In this case, the different colors distinguish the different chain lengths. The red color represents short-chain hydrocarbon compounds, the blue color represents medi-

Figure 4: Volume of tar yields

Table 2: Tar yields at 500°C without zeolite

Compounds		%
2-Amino-5-chloropyrimidine	$C_4H_4ClN_3$	4,77
Methanamine, hydrochloride	CH_6ClN	2,68
2-Pentanone	$C_5H_{10}O$	0,79
Formic acid	CH_2O_2	0,37
Acetic acid	$C_2H_4O_2$	17,34
Hydrazine, propyl-, ethanedioate	$C_5H_{12}N_2O_4$	0,6
Propanoic acid	$C_3H_6O_2$	0,24
2,4-Pentadienenitrile	C_5H_5N	0,37
3-Butene-1,2-diol	$C_4H_8O_2$	1,77
2-Furancarboxaldehyde	$C_5H_4O_2$	5,84
Pyridine, 2-methyl-	C_6H_7N	0,21
2-Cyclopenten-1-one	C_5H_6O	1,15
2-pentanone, 3-ethyl-	$C_7H_{14}O$	0,812
2-Furanmethanol	$C_5H_6O_2$	1,07
2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	0,62
n,n-diethylformamide	$C_5H_{11}NO$	0,394
2(5H)-Furanone	$C_4H_4O_2$	2,56
1,2-Cyclopentanedione	$C_5H_6O_2$	1,21
methyl-2-thiopene carboxylate	$C_7H_8O_2S$	0,397
2-Furancarboxaldehyde, 5-methyl-	$C_6H_6O_2$	0,7
2-Butanone, 3,3-dimethyl-	$C_6H_{12}O$	0,45
2-Cyclopenten-1-one, 3-methyl-	C_6H_8O	0,844
Phenol	C_6H_6O	0,43
Phenol	C_6H_6O	3,378
Furan, 2-butyltetrahydro-	$C_8H_{16}O$	0,84
2-Cyclopenten-1-one, 2-hydroxy-3-m	$C_6H_8O_2$	4,85
Phenol, 2-methyl-	C_7H_8O	0,66
Phenol, 2-methyl-	C_7H_8O	1,19

Compounds		%
Phenol, 3-methyl-	C_7H_8O	0,28
Phenol, 3-methyl-	C_7H_8O	4,51
Phenol, 2-methoxy-	$C_7H_8O_2$	1,31
Pentanal	$C_5H_{10}O$	0,82
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	$C_7H_{10}O_2$	0,8
Phenol, 2,4-dimethyl-	$C_8H_{10}O$	0,28
Phenol, 2,4-dimethyl-	$C_8H_{10}O$	0,45
Phenol, 3,4-dimethyl-	$C_8H_{10}O$	1,07
Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0,29
2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	1,93
1,2-Benzenediol	$C_6H_6O_2$	4,01
Phenol, 2-ethoxy-	$C_8H_{10}O_2$	0,28
Benzeneethanol, 2-methoxy-	$C_9H_{12}O_2$	1,37
2-Methoxy-4-vinylphenol	$C_9H_{10}O_2$	0,48
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	7,38
Benzaldehyde, 4-hydroxy-3-methoxy-	$C_8H_8O_3$	0,62
4-Methoxy-2-methyl-1-(methylthio)benzene	$C_9H_{12}O$	5,06
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_9H_{10}O_3$	0,53
2,3,5-trimethoxytoluene	$C_{10}H_{14}O_3$	3,504
Phenol, 2-methoxy-4-4propyl-	$C_{10}H_{14}O_2$	0,97
2,6-dimethyl-p-benzoquinon	$C_8H_8O_2$	1,078
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	0,44
2(1h)-pyrimidinone	C_5H_5NO	0,456
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	0,465
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	$C_9H_{10}O_4$	0,491
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	$C_{11}H_{14}O_3$	1,023
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphen	$C_{10}H_{12}O_4$	0,82
Desaspidinol	$C_{11}H_{14}O_4$	2,01

Table 3: Tar yields at 500°C with 25% zeolite

Compounds		%
Methanamine	CH_5N	1,04
Methanol	CH_3OH	7,31
Acetone	C_3H_6O	5,04
Acetic acid, methyl ester	$C_3H_6O_2$	0,83
Acetic acid	$C_2H_4O_2$	16,95
Acetic acid	$C_2H_4O_2$	26,13
2-butenal	C_4H_6O	0,47
2-Propanone, 1-hydroxy-	$C_3H_6O_2$	2,24
Propanoic acid	$C_3H_6O_2$	0,94
Propanoic acid	$C_3H_6O_2$	0,94
Propanoic acid	$C_3H_6O_2$	0,96
3-penten-2-one,	C_5H_8O	0,36
Propanoic acid, 2-methyl-	$C_4H_8O_2$	0,31
1-hydroxy-2-butanone	$C_4H_8O_2$	1,36
Ethanamine, N,N-dimethyl-	$C_4H_{11}N$	1,31
Cyclopentanone	C_5H_8O	0,98
Furfural	$C_5H_4O_2$	9,74
2-Butanone	C_4H_8O	0,63
2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	1,01
2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	1,13
Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	0,58

Compounds		%
Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	0,58
2(3H)-Furanone, dihydro-	$C_5H_8O_2$	0,43
1,3-Cyclopentanedione	$C_5H_6O_2$	0,6
Furfural	$C_5H_4O_2$	1,75
3-pentanone, 2-methyl-	$C_6H_{12}O$	0,29
Phenol	C_6H_6O	2,08
Propanoic acid, 2-methyl-	$C_4H_8O_2$	0,68
2-cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	1,16
2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	0,43
Phenol, 2-methyl-	C_7H_8O	0,83
Phenol, 4-methyl-	C_7H_8O	1,78
Phenol, 2-methoxy	$C_7H_8O_2$	2,28
Phenol, 2,4-dimethyl-	$C_8H_{10}O$	2,28
Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0,35
Phenol, 2-methoxy-4-dimethyl-	$C_8H_{10}O_2$	0,92
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0,59
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	2,31
2H-pyran-2,4(3H)-dione, 3-acetyl-6-methyl-	$C_8H_8O_4$	1,24
2,3,5-Trimethoxytoluene	$C_{10}H_{14}O_3$	0,7
Homovanilly alcohol	$C_9H_{12}O_3$	0,29
Tetraethylthiophene	C_9H_{12}	0,29
Desaspidinol	$C_{11}H_{14}O_4$	0,39

Table 4: Tar yields at 500°C with 25% zeolite

Compounds		%
Methanamine	CH_5N	1,04
Methanol	CH_3OH	7,31
Acetone	C_3H_6O	5,04
Acetic acid, methyl ester	$C_3H_6O_2$	0,83
Acetic acid	$C_2H_4O_2$	16,95
Acetic acid	$C_2H_4O_2$	26,13
2-butenal	C_4H_6O	0,47
2-Propanone, 1-hydroxy-	$C_3H_6O_2$	2,24
Propanoic acid	$C_3H_6O_2$	0,94
Propanoic acid	$C_3H_6O_2$	0,94
Propanoic acid	$C_3H_6O_2$	0,96
3-penten-2-one,	C_5H_8O	0,36
Propanoic acid, 2-methyl-	$C_4H_8O_2$	0,31
1-hydroxy-2-butanone	$C_4H_8O_2$	1,36
Ethanamine, N,N-dimethyl-	$C_4H_{11}N$	1,31
Cyclopentanone	C_5H_8O	0,98
Furfural	$C_5H_4O_2$	9,74
2-Butanone	C_4H_8O	0,63
2-Propanone, 1-(acetyloxy)-	$C_5H_8O_3$	1,01
2-Cyclopenten-1-one, 2-methyl-	C_6H_8O	1,13
Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	0,58

Compounds		%
Ethanone, 1-(2-furanyl)-	$C_6H_6O_2$	0,58
2(3H)-Furanone, dihydro-	$C_5H_8O_2$	0,43
1,3-Cyclopentanedione	$C_5H_6O_2$	0,6
Furfural	$C_5H_4O_2$	1,75
3-pentanone, 2-methyl-	$C_6H_{12}O$	0,29
Phenol	C_6H_6O	2,08
Propanoic acid, 2-methyl-	$C_4H_8O_2$	0,68
2-cyclopenten-1-one, 2-hydroxy-3-methyl-	$C_6H_8O_2$	1,16
2,3-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	0,43
Phenol, 2-methyl-	C_7H_8O	0,83
Phenol, 4-methyl-	C_7H_8O	1,78
Phenol, 2-methoxy	$C_7H_8O_2$	2,28
Phenol, 2,4-dimethyl-	$C_8H_{10}O$	2,28
Phenol, 2,3-dimethyl-	$C_8H_{10}O$	0,35
Phenol, 2-methoxy-4-dimethyl-	$C_8H_{10}O_2$	0,92
Phenol, 4-ethyl-2-methoxy-	$C_9H_{12}O_2$	0,59
Phenol, 2,6-dimethoxy-	$C_8H_{10}O_3$	2,31
2H-pyran-2,4(3H)-dione, 3-acetyl-6-methyl-	$C_8H_8O_4$	1,24
2,3,5-Trimethoxytoluene	$C_{10}H_{14}O_3$	0,7
Homovanilly alcohol	$C_9H_{12}O_3$	0,29
Tetraethylthiophene	C_9H_{12}	0,29
Desaspidinol	$C_{11}H_{14}O_4$	0,39

um-chain hydrocarbon compounds, while the yellow color represents long-chain hydrocarbon compounds.

Table 2 shows the proportion of tar yield compounds resulted from the pyrolysis of mahogany wood at 500 °C without zeolite. It can be seen that the compounds formed have carbon chain lengths from C_1 to C_{11}, comprising 20.63% short-chain hydrocarbons, 37.29% medium-chain hydrocarbons, and 42.08% long-chain hydrocarbons. Meanwhile, Table 3 displays the generated tar yields at 500 °C with 25% zeolite. It produces the same range of carbon chain length as the pyrolysis without zeolite, i.e., the carbon chain lengths formed range from C_1 to C_{11}. However, note that the percentage of carbon chain lengths differs from the previous one. 62.38% have short carbon chains, 24.87% with medium-chain carbon, and 12.75% with long carbon chains. Table 4 illustrates the tar yields components with the addition of 50% zeolite. It can be seen that the compounds of tar yields formed have carbon chain lengths spanning from C_1 to C_{15}, with the percentage of compounds consisting of 43.33% short-chain carbon, 43.96% medium-chain carbon, and 12.71% long-chain carbon.

If the lengths of the carbon chain are compared among others as shown in Figure 5, the pyrolysis with 25% zeolite produced the shortest chain compounds of them all. This is because, in the lignocellulose structure, the C-O and C-C bonds breaks down and results in Brønsted and Lewis acid-base reactions. As a result, zeolite is
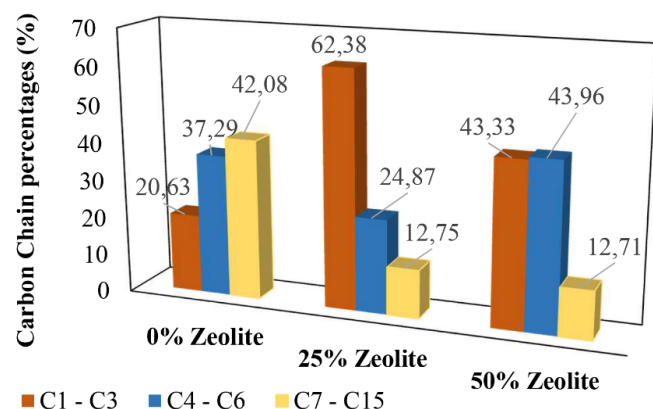

Figure 5: The percentages of tar yields' Carbon chain

then able to receive the H+ ions released by the biomass during the pyrolysis process. As increase pyrolysis temperature, as much more biomass decomposed. It affects the cracking of long-chain hydrocarbons which are split into shorter-chained hydrocarbon compounds.

As it turns out, the addition of 50% zeolite can produce the most medium-chain carbon compounds than others. The abundant Medium-chain carbon in tar yields are caused by the catalytic cracking process in which zeolites produce aromatic compounds through the aromatization process of the already formed alkene compounds [13] classified as Medium-chain carbon compounds due to β scission process that will be explained in the next section below.

During the pyrolysis process, as the pyrolysis temperature increases, the aromatic components increase as well. Then, by measuring the tar yields compounds, we can prove that zeolite is able to decompose hydrocarbons in biomass from longer-chained carbons to shorter-chained ones. Furthermore, the tar formation mechanism that occurs as shown by the GC-MS test results will be explained further below.

The effects of zeolite on the mechanism of pyrolysis cracking during the formation of tar yields

Making use of the GC-MS method, this study examined the production of tar yields through the pyrolysis of mahogany wood under the influence of zeolite. Zeolite acted a catalyst that assists the cracking process of hydrocarbon chains, involving the Brønsted and Lewis acid-base reactions. These acid-base reactions occur when the lignocellulose structure breaks down the C-C and C-O bonds and when the gas product moves through the zeolite pores, breaking down long-chain hydrocarbons into shorter ones. There are three stages in which zeolite is involved in the breaking of hydrocarbon chains, which are initiation, propagation, and cracking (β scission).

The initiation stage consists of the formation of carbenium ion or positively-charged hydrocarbon compounds, wherein the alkene hydrocarbons either receive H+ ion at the Brønsted site or release H+ ions at the Lewis site. The propagation stage consists of the exchange of H+ ions in the alkanes adjacent to the carbonium ions, turning carbonium ions into alkanes, and vice versa.

The final step in the cracking of hydrocarbon chains by zeolites is the β scission process. In this process, the carbonium ions formed in the propagation process are split into new carbonium ions and alkenes with shorter chains. This breaking process occurs continuously to produce hydrocarbons with shorter chains. After the process of breaking the hydrocarbon chain takes place, the aromatization process occurs, which is the process of forming aromatic compounds by alkene compounds that have been formed from the catalytic cracking process.

The steps of the biomass cracking mechanism are illustrated graphically in Figure 6 using the HyperChem simulation. It shows that the formation mechanisms of tar yield are due to the zeolite effect. It can be seen that the pyrolysis process causes the formation of shorter compounds from more complex biomass compounds; cellulose, hemicellulose, and lignin. The breakdown of cellulose without zeolite only involves thermal cracking process, so furan compounds and some acidic compounds are formed. Whereas, in the cracking of cellulose with the help of 25% and 50% zeolite, the catalytic cracking process begins by breaking down furan compounds into alkenes, followed by the aromatization process.

In the breakdown of hemicellulose compounds without zeolites—similar to cellulose—the thermal cracking process also produces only furan compounds and acidic compounds. However, in the breakdown of hemicellu-
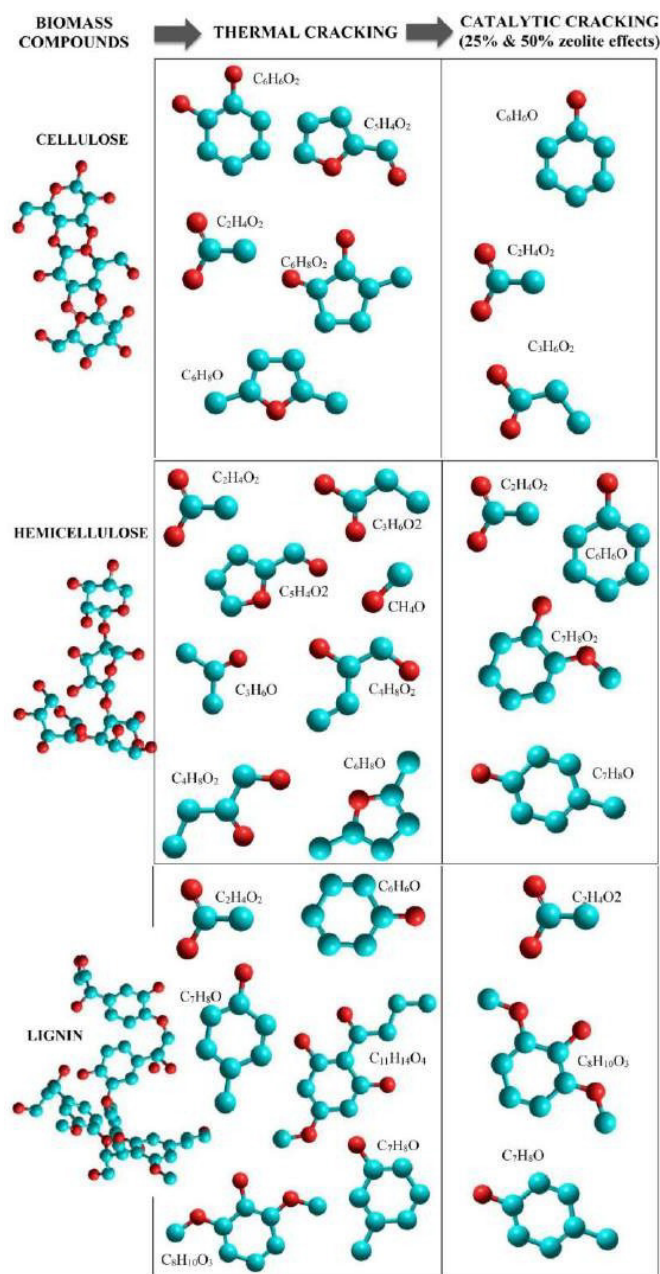
Figure 6: The chemical mechanism formations of tar yields

lose with 25% and 50% zeolite, it also forms furan compounds and then produces aromatic compounds and alkenes. Lastly, this study will discuss the pyrolysis process of lignin. In the absence of zeolite, the dissociation process of hydrocarbon chains only involves thermal cracking, which forms aromatic and acidic compounds. It is only after adding both 25% and 50% zeolite that the process also takes catalytic cracking into account. The catalytic cracking serves to break the C-O and C-C bonds in the lignin structure due to its stronger bonds. However, this study believes that the pyrolysis of lignin has no effect on the overall gas products because of its rich aromatic compounds with a much larger molecular size compared to the zeolite pores. The difference in size prevents the gas to pass through the zeolite pores.

CONCLUSION

After investigating the mechanism formation of tar yields in the pyrolysis process with the help of zeolite as a catalyst, it can be concluded that:

1. The volume of tar yields increased significantly with the addition of zeolite catalyst because the biomass decomposition was affected by both thermal cracking and catalytic cracking;

2. The catalytic process reveals that the more zeolite was added, the shorter the carbon chain of the produced tar, whereas the volume of the tar yields increases;

3. This study found similarities in the formation of tar through the thermal and catalytic cracking with the Brønsted-Lowry and Lewis acid-base reactions.

The mahogany wood component, cellulose, turned furan compounds into alkenes. Hemicellulose converts furan compounds into aromatic compounds and alkenes. Then, lignin was decomposed into aromatic and acidic compounds.

REFERENCES

1. Kan, T., Strezov, V., Evans, T., He, J., Kumar, R., Lu, Q. (2020). Catalytic pyrolysis of lignocellulosic biomass: A review of variations in process factors and system structure. Renewable and Sustainable Energy Reviews, vol. 134, DOI: 10.1016/j.rser.2020.110305

2. Yanga, H., Yaoa, J., Chena, G., Maa, W., Yana, B., Qi, Y. (2014). Overview of upgrading of pyrolysis oil of biomass. Energy Procedia, vol. 61, 1306–309, DOI: 10.1016/j.egypro.2014.11.1087

3. Busca, G. (2017). Acidity and basicity of zeolites: A fundamental approach. Microporous and Mesoporous Materials, vol. 254, 3-16, DOI: 10.1016/j.micromeso.2017.04.007

4. Li, G., Pidko, E., A. (2018). The Nature and Catalytic Function of Cation Sites in Zeolites: a Computational Perspective. ChemCatChem Review, 134-156, DOI: 10.1002/cctc.201801493

5. Kostyniuk, A., Bajec, D., Likozar, B. (2020). Catalytic hydrogenation, hydrocracking and isomerization reactions of biomass tar model compound mixture over Ni-modified zeolite catalysts in packed bed reactor. Renewable Energy, DOI: 10.1016/j.renene.2020.11.098

6. Ahmed, T., Xiu, S., Wang, L., Shahbazi, A. (2018). Investigation of Ni/Fe/Mg zeolite- supported catalysts in steam reforming of tar using simulated-toluene as model compound. Fuel, vol. 211, 566-571, DOI: 10.1016/j.fuel.2017.09.051

7. Wei, B., Jin, L., Wang, D., Xiong, Y., Hu, H., Bai, Z. (2020). Effect of different acid- leached USY zeolites on in-situ catalytic upgrading of lignite tar. Fuel, vol. 266, DOI: 10.1016/j.fuel.2020.117089

8. Kong, X., Bai, Y., Yan, L., Li, F. (2016). Catalytic upgrading of coal gaseous tar over Y- type zeolites. Fuel, vol. 180, 205-210, DOI: 10.1016/j.fuel.2016.03.101

9. Ahmed, T., Xiu, S., Wang, L., Shahbazi, A. (2020). Chapter 5 - FCC catalysts. Sadeghbeigi, R., Fluid Catalytic Cracking Handbook (Fourth Edition) An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units, Butterworth-Heinemann publisher, 83-110, DOI: 10.1016/C2016-0-01176-2

10. Yan, L., Liu, Y., Lv, P., Wang, M., Li, F., Bao, W. (2020). Effect of Brønsted acid of Y zeolite on light arene formation during catalytic upgrading of coal pyrolysis gaseous tar. Journal of the Energy Institute, vol. 93, no. 6, 2247-2254, DOI: 10.1016/j.joei.2020.06.007

11. Kühl, Günter H. (1999). Modification of Zeolites. Weitkamp, J., Puppe, L. Catalysis and Zeolites Fundamentals and Applications. Springer-Verlag, Berlin, 81-197

12. Wijayanti, W., Tanoue K. (2013). Char formation and gas products of woody biomass pyrolysis. Energy Procedia, vol. 32, 145-152, DOI: 10.1016/j.egypro.2013.05.019

13. Yang, H., Yan, R., Chen, H., Lee, H., D., Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, vol. 86, no. 12-13, 1781-1788, DOI: 10.1016/j.fuel.2006.12.013

14. Wijayanti, W., Tanoue, K., Suetomi, T. (2011). Rule of thumb for simulating biomass pyrolysis in packed bed reactor. 11AIChE - 2011 AIChE Annual Meeting, Conference Proceedings

15. Park, J., Lee, Y., Ryu, C. (2016). Reduction of primary tar vapor from biomass by hot char particles in fixed bed gasification. Biomass and Bioenergy, vol. 90, 114-121, DOI: 10.1016/j.biombioe.2016.04.001

16. Rahimi, N., Karimzadeh, R. (2011). Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review. Applied Catalysis A: General, vol. 398, no. 1-2, 1-17, DOI: 10.1016/j.apcata.2011.03.009