Catalytic Hydrothermal Liquefaction of Jatropha Curcas Using KCC-1 Catalyst

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ABSTRACT

In this paper, the KCC-1 catalyst on the production of bio-oil was investigated. The objective is to find the effect of the catalyst on the yield and compound in the bio-oil. Catalytic hydrothermal liquefaction was applied by setting temperature of 350℃, biomass to solvent ratio of 1:4, reaction time of 60 min and 10 wt% of catalyst loading. From the experimental work, the oil yield was reduced 21.9% when catalyst was used. The results also showed that the bio-oil produced by using KCC-1 was mainly composed of esters. From these results, it can be concluded that KCC-1 could be potential catalyst to improve the quality of bio-oil.

Keywords: Hydrothermal liquefaction, oil seed, bio-oil, catalyst, methyl ester.

1. INTRODUCTION

In recent years, fossil fuels have been used and be the most important energy source in the world. Its consumption has been increased considerably which cause some issues related to energy consumption demand, depleted of hydrocarbon reserves and, the most important issue is the environmental pollution by greenhouse gas emission due to hydrocarbon combustion [1–3]. Thus, several researchers have developed alternative methods to substitute fossil fuels into other renewable and sustainable fuels such as bio-fuels. Bio-fuel is a mixture of water and organic liquids, which contains carboxylic acids, aldehydes, phenols, ketones, and others [4], which is produced from biomass. Biomass is a sustainable and renewable energy resources. The modification of biomass to biofuel and its additionally implementation release CO_2 into the atmosphere, which is absorbed through continuous photosynthesis during plant growth, thus assisting lower carbon emissions [5–7]. Among all types of biomass, using non-food seed biomass as feedstock has become an important element in biodiesel production [8].

Biomass that converted into bio-fuel by hydrotreating process such as hydrothermal liquefaction (HTL). HTL is a promising technology for conversion of biomass into biofuels. Products from HTL process depend on the operating conditions such as pressure, temperature, biomass to solvent ratio and reaction time. HTL is suitable for handling wet biomass with varying moisture contents, thus reducing energy for drying process [9]. Unlike other processes, hydrothermal liquefaction uses water as the reaction medium and catalyst. Therefore, this is an ideal process for biomass with a high moisture content [10]. At conditions close to the critical point, water has various interesting properties. The conditions of subcritical water as an excellent medium for fast, homogeneous, and efficient reactions due to its low viscosity and high solubility of organic substances [11-13]. Consequently, during the last decades, there has been a strong interest in using subcritical water as a solvent and reaction medium for biomass conversion. Subcritical water behaves very differently not only from water at room temperature but in some aspects also from supercritical water. Heger *et al.* [11] have reported that the dielectric constant decreases from 78 F m^{-1} at 25°C and 0.1 MPa to 14.07 F m^{-1} at 350°C and 20 MPa [11]. This gives rise to increased solubility of hydrophobic organic compounds, such as free fatty acids [14-15]. On the other hand, the solubility of salts decreases significantly.

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However, corrosion in the subcritical water environment is a critical issue. Acidic and oxidizing conditions can cause rapid corrosion, and this can be even more severe at subcritical conditions than at supercritical conditions, due to the relatively dense and polar character of subcritical water [16]. Thus, a catalyst has been used to overcome this issue. The design and development of efficient heterogeneous catalysts with a good stability for the transesterification reaction have been an emergent and challenge field of research. On the other hand, A mesoporous silica catalyst which have high surface area have recently received great attention on which the catalytically active species can be highly dispersed, thereby improving the catalytic performance [17]. Previous work by Samart *et al.* [18] has suggested that calcined potassium iodide supported on mesoporous silica as the catalyst for transesterification of soybean oil to biodiesel gave the highest conversion yield, attaining nearly 95%.

Fibrous nano-silica (KCC-1), which features a high surface area and easy accessibility through its fibers (as opposed to the traditional use of pores), is reported by Polshettiwar *et al.* [19] This would be an ideal catalyst that exhibit high accessibility of active sites and excellent catalytic activity for increased high quality of bio-fuels. Thus, in this article, we investigated the effect of using KCC-1 catalyst on the quality of bio-fuels under hydrothermal liquefaction of Jatropha curcas.

2. EXPERIMENTAL PROCEDURE

2.1 Biomass and Catalyst Preparation

Jatropha curcas seeds were collected around Perlis state. The seeds were washed to clean up dirty and impurities. Then, this biomass was oven-dried at temperature of 105°C for 24 hours. The seeds were punched using mortar and pestle to separate its kernel and husk. Parent KCC-1 was prepared by microwave assisted hydrothermal method as described by Hamid *et al.* [20]. Concisely, two solutions were prepared. Solution 1 was prepared by mixing tetraethyl orthosilicate, cyclohexane and 1-pentanol in the ratio of 1:23.08:1.08 and those solution was stirred in a Teflon Bottle. Otherwise, solution 2 was prepared by mixing cetylpyridinium bromide and urea in ratio of 0.22:0.83 in a distilled water and this solution were added into solution 1. The mixture then was stirred for 30 min in room temperature and subjected into intermittent MW irradiation at 400W for 4h. The resultant was then cooled, centrifuged, and rinsed with water. Next, it was dried overnight at 109.85°C and calcined for 6h at 549.85°C.

2.2 Catalytic Hydrothermal Liquefactio

For liquefaction process, a 5g of Jatropha Curcas was loaded into the stainless-steel reactor model CJF-0.1L, and followed by several amount of water. The liquefaction process was run according to the setting temperature of 350°C, biomass to solvent ratio of 1:4 and reaction time of 60 min according to the previous research that obtained optimum condition of oil yield. The optimum condition was then being used for further experiment using 10 wt% of KCC-1 catalyst. Then, reactor was cooled down to ambient temperature. The reacted products, which were solid and liquid were washed with approximately 150 ml DCM and transferred into the conical flask. Heavy oil can be described as the oil product from liquefaction process which has a density of greater than one, while light oil has a density less than one. The solid residue was separated from the liquid product by filtration with filter paper. The filtered liquid product was left dried in the fume cupboard. The obtained crude oil was measured and recorded.

2.3 Yields and Characterization of Products

The products were washed and separated according to the explanation before. Conversion and oil yield were then calculated using equation (1), (2), and (3) below [21];

$$\text{Char yield} = \frac{\text{mass char (g)}}{\text{initial sample loaded (g)}} \text{ x } 100 \tag{1}$$

$$\text{Oil yield} = \frac{\text{mass of bio-oil (g)}}{\text{mass of biomass (g)}} \text{ x } 100 \tag{2}$$

$$\text{Gas yield} = 100 - \text{Char yield} - \text{Oil yield} \tag{3}$$

Gas chromatography–mass spectrometry (GC MS – QP2010 Ultra Shimadzu) analyses of the oils (1 µL in DCM) were performed (source temperature 280 °C). Separation was performed on a fused silica capillary column (30 m × 0.25 mm i.d) coated with BPX5 phase (0.25 µm thickness). Helium was used as the carrier gas, with a temperature programme of 35 °C (2 min) to 250 °C at 20 °C/min and hold for 20 min. Injections were performed in full scan mode with split ratio 1:30. Experiments were repeated 3 times for its reproducibility.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis of KCC-1

The crystalline structure of the KCC-1 catalyst was examined by powder XRD.The obtained nanosilica KCC sample is presented in Figure 1. The broad characterisctic peak centered about 22-23˚, correlate to the amorphous silica [22]. The XRD pattern demonstrate the successful synthesis of KCC material. The crystallite size of the sample was calculated using Scherrer equation: It was found that crystallite size for this sample was 8.84nm. Previous studied by Prabhu *et al.* [23] also found the same peak and the crystallite size of the sample of KCC-1 was 8.83nm.

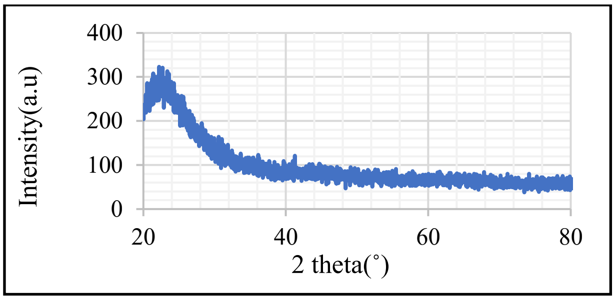

Figure 1. XRD of KCC-1.

3.2 Product Yields

Table 1 showed the percentage of oil yield, char yield and gas yield. It showed that the percentage of oil yield without using catalyst is higher, however decrease as much as 21.9% when using KCC 1 catalyst. Polshettiwar *et al.* [19] and Teh *et al.* [24] found that KCC 1 has high surface area and strong acid sites which showed high catalytic activity toward hydrocracking.

Table 1 Percentage of products yield for non-catalytic and catalytic bio-oil at ratio of 1:4, temperature of 350°C, and reaction time of 60 min

	Oil yield (%)	**Char yield (%)**	**Gas yield (%)**
Non-catalytic	68.7	0.22	31.08
Catalytic	46.8	0.62	52.58

The decreasing in oil yield was due to the excessive cracking by the catalyst as the result of char and gas yield increased after catalyst was added into the reaction. A part from that, the reduction of oil yield after addition of catalyst attributed to the increased generation of condensable gases inside the reaction system as can be seen in the result of the gas yield.

3.3. Characterization of Oil Yields

3.3.1 GCMS Analysis

Characterization of oil yield has been investigated in this studied as we focus on the quality of the bio-oil after adding KCC 1 catalyst. As can be seen in Figure 2., ester compound was increased 13.6% after using KCC-1 catalyst, whereas the percentage of acid compound was decreased 7.9%. Figure 2 also showed the results of hydrocarbon dan alcohol content. Both compounds were slightly decreased after the addition of KCC-1 catalyst. Previous studied by Qureshi *et al.* [25] reported that KCC-1 can act as catalyst support for transfer hydrogenation of alkene. Besides, this mesoporous silica catalyst also acts as good hydrogen storage.

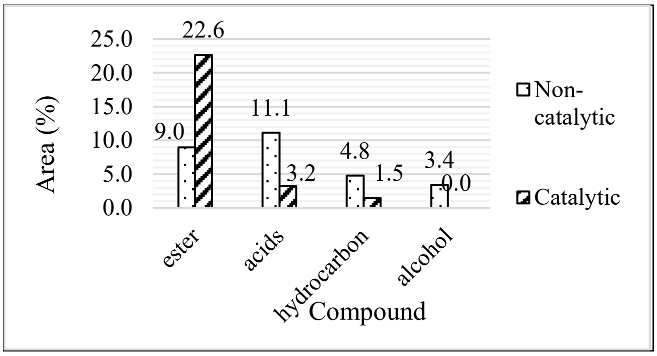

Figure 2. GCMS analysis of non-catalytic and catalytic bio-oil.

The hydrocarbon content was decreased due to the dehydrogenation of hydrocarbon for production of hydrogen. The produced hydrogen then was bound and stored by the catalyst for another reaction or can be used as another alternative source of energy. Furthermore, the reducing of alcohols and acids compound were due to the esterification process to form ester. When catalyst was presented in the reaction, the formation of ester was accelerated by the binding of H and react with oxygen to form water.

4. CONCLUSION

This study explored the effect of KCC-1 catalyst on the production of bio-oil by hydrothermal liquefaction of Jatropha curcas with water as a solvent. The result showed that with subcritical condition of water and presence of catalyst, the oil yield decreased. However, the ester compound increased with reducing of acid compound. This showed that KCC-1 can be a good catalyst to improve the bio-oil quality.

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