Hydroprocessing of Rubber Seed Oil over Ni-Mo/γ-Al$_2$O$_3$ for the Green Diesel Production

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Hydrodeoxygenation is most considered route for up-gradation of biodiesel and triglycerides towards direct conversion into diesel range hydrocarbon (green diesel). Heterogeneous (Ni-Mo/γ-Al$_2$O$_3$ catalysts) catalysis offers more promising routes for transformation of biomass into value added bio-chemicals more likely selective hydrocarbons in a resourceful approach. In this study, the Ni-Mo/γ-Al$_2$O$_3$ type catalysts were investigated for the hydrodeoxygenation of rubber seed oil for the diesel range hydrocarbons (*n*-C15-*n*-C18). Monometallic solid acid catalysts (Ni/γ-Al$_2$O$_3$) and bimetallic (Ni-Mo/γ-Al$_2$O$_3$) catalysts were tested for HDO reaction at 340 °C, 21 bar, H$_2$/oil ratio 150 Nm^3/m^3 using 5 g, WHSV = 10 h^{-1} for 5 h time on stream in tubular fixed bed reactor (pilot scale). Among the sonochemically synthesized catalysts, 3 wt. % Ni/γ-Al$_2$O$_3$ showed the higher catalytic activity up to 15.4 wt. % and bimetallic Ni-Mo/γ-Al$_2$O$_3$ was perceived to be more active with 15.35 wt.% diesel range (C15-C18) hydrocarbons from rubber seed oil. The selectivity for *n*-C15-*n*-C18 hydrocarbons were determined as C15 (7.14 %), C16 (7.16 %), C17 (0.42%) and C18 (0.78%) among the liquid alkanes. The product distribution revealed that the reaction proceeded mainly with decarboxylation (DCO$_2$) and decarbonylation (DCO) with high C15/C16 ratio. The results from hydrodeoxygenation of rubber seed oil showed an innovative reaction path for the production of diesel range hydrocarbons. The monometallic 3 wt.% Ni/Al$_2$O$_3$ and 15 wt.% Ni/Al$_2$O$_3$ synthesized via conventional method showed lower triglycerides conversion with 63 wt.% and 70 wt.% respectively. All the sonochemically synthesized catalysts revealed complete conversion of triglycerides (99 wt.%) into other paraffin, olefins and oxygenates and showed better activity even at low operational parameters for hydrodeoxygenation of triglycerides present in rubber seed oil.

1. Introduction

Hydroprocessing of vegetable oil is well-developed technique for green diesel production widely investigated on various feedstock. Several feedstocks have been used for conversion of biomass in to diesel range hydrocarbons and biodiesel. Such as sunflower oil (Marco et al., 2016), rapeseed oil (Kukushkin et al., 2015), algal oil (Song et al., 2013), soybean oil (Urzhuntsev et al., 2016) palm oil (Wang et al., 2015) and jatropha oil (Hwang et al., 2016). All the feedstock treated for hydroprocessing provoked an argument food vs. fuel. Non-edible triglycerides, such as jatropha oil has been extensively investigated for trans-esterification (Bokhari et al., 2016) and as well as hydrodeoxygenation (Yasir et al., 2016). Beside the availability of Jatropha oil, extensive research has been focused on rubber seed oil for trans-esterification (Chuah et al., 2016). Rubber seed oil poses high free fatty acids more suitable for biodiesel production (Reshad et al., 2015). Nevertheless, rubber seed oil still not reported for hydrodeoxygenation for the production of diesel range hydrocarbon. Heterogeneous solid acid catalysts play an important role for hydrodeoxygenation of various oxygenates. The activity and selectivity depends on acidity of support and metal loading, surface area, particle size, homogenous dispersion. The effect of promoter and proper synthetic method also enhanced the catalytic reactions (Tran et al., 2014). Ni-Mo/γ-Al$_2$O$_3$ type catalysts were investigated for various feedstock for high selectivity (Sotelo-Boyás et al., 2010). Ni/γ-Al$_2$O$_3$ is most common hydrogenating catalyst found to be more active with high deoxygenating ability. Mo/γ-Al$_2$O$_3$ alone has been

investigated for hydrodeoxygenation of various feedstock with high selectivity and higher conversion and more suitable for mainly HDO route (Kumar et al., 2010). The synergic effect of Ni and Mo with solid acid support enhanced the conversion from triglyceride to hydrocarbon via DCO, DCO_2, and HDO routes as shown in Eq(1-3). The hydroprocessing steps involved hydrogenolysis of triglycerides followed by the formation of fatty acids, onward two different routes as decarboxylation (DCO_2), and decarbonylation (DCO) as mentioned in following Eq(1-3). R denotes an alkyl group contain mainly C18 chain atoms.

$$R\text{-}COOH + 1H_2 \longrightarrow R\text{-}H + 1H_2O + CO_2 \tag{1}$$

$$R\text{-}COOH + 0H_2 \longrightarrow R\text{-}H + 0H_2O + CO_2 \tag{2}$$

$$R\text{-}COOH + 3H_2 \longrightarrow R\text{-}CH_3 + 2H_2O \tag{3}$$

The proper synthesis of catalysts also has a great compatibility to enhance the activity of catalysts. The most common techniques to prepare solid acid catalysts are wet impregnation method, hydrothermal, sol gel method, and microwave and sonochemical methods. Most of the catalysts have been used before for HDO of vegetable oil were commercial or impregnated using conventional methods. The foremost effects for synthesis of catalysts using sonochemical method are catalytic activity, higher specific surface area, homogenously metal scattering and smaller crystallite size due to acoustic cavitation (Vafaeian et al., 2013). These properties improve the catalyst for more outstanding catalytic process. Nevertheless, sonochemically synthesize catalyst has been reported for hydrodesulphurization of model compounds and some other applications. This is evidenced from reported studies that the catalytic activity of sonochemically-formulated catalysts can retain the activity for longer time than wet impregnation method (Ramos et al., 2008). Ramos et al (Ramos et al., 2008) studied the effects of sonication on Co, Ni, Co-Mo and Ni-Mo type catalysts for the hydrodesulphurization (HDS) of thiophene. Likewise, the formation of bimetallic solid acid catalysts using ultrasound-assisted method can play a significant role in hydrodeoxygenation (HDO) of non-edible oil to hydrocarbons. The higher surface area, pore volume and pore size that offers the more space for long chain fatty acids and triglycerides for hydrodeoxygenation reaction. As rubber seed oil differs in composition of fatty acids with other vegetable oil, the extensive investigation is needed. The hydrodeoxygenation over sonochemically synthesized solid acid catalysts have not been reported with rubber seed oil. This paper discussed some preliminary investigation on hydrodeoxygenation of rubber seed oil for diesel range hydrocarbons in terms of individual alkanes produced and triglycerides conversion at low temperature, pressure and limited hydrogen using non-sulfided sonochemically synthesized catalysts.

2. Methodology

2.1 Catalyst synthesis and Characterization techniques

The monometallic 3 wt.% Ni/ γ-Al2O3 (3NA), 12 wt.% Ni/ γ-Al2O3 (12NA), 15 wt.% Ni/ γ-Al2O3 (15NA), and bimetallic solid catalysts 12 wt. % Ni 3 wt. % Mo/ γ-Al2O3 (12N3MA) were synthesized by conventional wet impregnation method (WI) and sonochemical method (Us) as reported earlier (Ameen et al. 2016a,b). All the synthesized catalysts were characterized as reported in our previous work (Ameen et al. 2016 a, Ameen et al. 2016 b). To diagnose the surface metal oxides the X-ray Diffraction (XRD) pattern, the field emission electron microscopy (FESEM) techniques, EDX-Dot mapping analysis, Surface area BET, pore volume and pore size, Transmission Electron Microscopy (TEM) of all the sampled were determined and reported earlier (Ameen et al., 2016a,b).

2.3 Catalysts activity (Hydrodeoxygenation)

The rubber seed oil (RSO) hydroprocessing was conducted in fixed bed tubular reactor (down flow). Approximately 5 g of catalyst was loaded into catalyst bucket to make a catalyst bed using quartz wool. Feedstock (RSO) was proceeded with preheated and vaporized and fed with H_2 (20 % Balanced in N_2) stream from top to bottom. Catalysts were reduced in situ at 450 °C with 20% H_2 balance with N_2 hydrogen flow 50 mL/min for 3 h at 30 bar. RSO hydrodeoxygenation was conducted after activating the catalysts under 21 bar pressure at 340 °C, H_2/oil 150 N cm^3/cm^3, WHSV = 10, all the catalysts were tested for 5 h times on stream. The products were condensed via condenser. Gas and liquid products were separated in gas-liquid separator and collected in receiver pot. The liquid product was collected after interval of 1 h. As the reaction conditions stabilized, the liquid samples were collected from reservoir for further analysis. The liquid products were analysed using offline gas chromatography (GC) equipped with capillary column (MXT-1HT) (10 m, 0.53 mm ID, 2.65 µm) with Flame Ionization Detector (FID) according to ASTM D2887 Method. Gas chromatography

attached with mass detector (GC-MS) was used to confirm the product composition and intermediates. ASTM D6258 method was used to determine the triglycerides amount in reaction mixture. The detailed analysis of catalysts performance was determined with product yield and triglycerides conversion. The product composition was determined theoretically based on % area of *n*-alkane and external calibration curve for (C15-C18).

3. Results and Discussion

3.1 Hydrodeoxygenation

The effect of ultrasound irradiation on synthesis of solid acid catalysts and their catalytic activity for the hydrodeoxygenation of rubber seed oil (RSO) was investigated. The catalytic performance was studied in terms of diesel range hydrocarbon (C15-C18) % yield, hydrodeoxygenation (HDO), decarboxygenation (DCO_2) and decarbonylation reactions (DCO), reaction pathways and triglycerides conversion to smaller alkanes, alkenes and other oxygenates. The HDO reactions were performed with RSO over 3NAWI, 3NAUs, 12NAWI, 12NAUs, 15NAWI, 15NAUs, 12N3MAWI and 12N3MAUs catalysts. In addition, similar study was performed to consider the effect of sonochemically synthesized 3NAUs catalyst at the same reaction condition as Harnos (2012) has reported with sunflower oil using non-sulphided monometallic 3 wt.% $Ni/\gamma-Al_2O_3$ catalyst. RSO contains high acid value and high free fatty acids with unsaturated triglycerides (triolein). The triglycerides partially followed the HDO, DCO_2 and DCO reaction pathway to produce *n*-alkanes (pentadecane, hexadecane, heptadecane and octadecane). In terms of synthetic methods of catalysts with same amount and metal compositions, the HDO/ DCO_2/DCO activity increased with sonochemically-synthesized catalyst as shown in Figure 1. Sonochemically synthesized 3NAUs catalysts showed a significant yield among the monometallic catalysts. It has been observed that with the increase of Ni loading no significant effect occurred on the hydrocarbons yield. Almost, all the catalysts showed similar diesel range hydrocarbons on the same reaction condition. This might be due to the reaction proceeded at higher temperature as all the triglycerides above 280 °C typically converted in fatty acids and glycerol (hydrogenolysis). These fatty acids on further hydrogenation in the presence of Ni catalysts converted into fatty alcohols and aldehydes followed by dehydrogenation with removal of water molecules. Fatty aldehydes or fatty acids at high temperature pressure follow the decarbonylation and decarboxylation route to produce mainly CO and CO_2 as by product respectively. In the presence of limited H_2, Ni being hydrogenating catalyst did not follow the HDO route and reaction mainly followed by DCO_2 and DCO that was confirmed by the presence of CH_4 in gaseous mixture which was the main product of CO/CO_2 and H_2 (methanation reaction) (Krár et al., 2010) and more recently (Kumar et al., 2014). However, sonochemically synthesized bimetallic (12N3MAUs) showed higher yield comparatively conventionally synthesized catalysts. In addition, the Mo is mainly follow the hydrodeoxygenation reaction pathway, the addition of Mo as promoter in bimetallic solid acid catalysts modified the reaction pathway due to formation of different intermediates such as octadecanon instead of octadecanol. The complex composition of triglycerides and free fatty acid present in rubber seed oil followed more than one reaction pathway which can be proposed by presence of various intermediates in reaction mixture as reported by (Kumar et al. 2014).
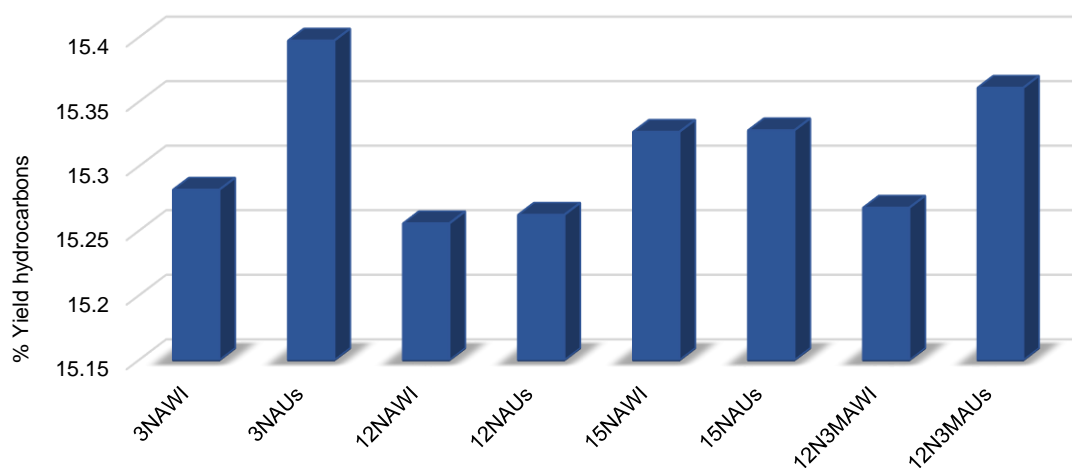

Figure 1: HDO yield of rubber seed oil for diesel range (C15-C18) hydrocarbons over sonochemically synthesized and conventionally synthesized catalysts.

3.2 Product distribution

The product distribution in the result for HDO of rubber seed oil revealed that conventionally synthesized catalysts led more hydrocracking product compared to sonochemically-synthesized catalysts. Nevertheless, the 12N3MAUs catalysts was observed to be active with higher yield for C15 (7.15 %), C16 (7.19 %) C17 (0.33 %) and C18 (0.72 wt. %) as shown in Figure 2 (a). The HDO reaction of RSO mainly produced C15 and C16 hydrocarbons with other intermediates. The DCO and DCO_2 reaction pathway was mainly followed by RSO due to low operational parameters such as low pressure, high temperature, low H_2/oil ratio and higher WHSV. As limited hydrogen consumption led the reactions as illustrate in Eq. (1-2) producing lower chain *n*-paraffin, though higher H_2 consumption favours the hydrodeoxygenation pathway as stable intermediates required excess of H_2. The comparative studies on both type of synthesized catalysts showed almost similar hydrocarbon yield. However, the isomerization and higher alkanes such as eicosane (C20), nondecane (C19) were observed higher in sonochemically-synthesized catalysts as illustrated in Figure 2 (b). The conventionally synthesized catalysts led more towards hydrocracking smaller paraffin in the range of (C9-C14). The gaseous products were analysed only for CO, CO_2, and CH_4 using GC-TCD that was confirmed by the presence of CH_4. The contribution of HDO and formation of C16/C18 (C16 7.16% and C18 0.79%) was found higher in all sonochemically synthesized catalysts. The formation of C16 and C18 in sonochemically-synthesized catalysts was significant as shown in Figure 3. However, the major changes have been observed in DCO/ DCO_2 ratio lower than C16/C18 ratio in both type of synthesized catalysts, these results are consistent with (Kubicka et al., 2010). The overall hydrocarbon produced over sonochemical synthesized catalysts are as follows (C16 > C15 > C18 > C17) that shows major routed followed for HDO >DCO>DCO_2. However, catalysts synthesized via wet impregnation produced hydrocarbons as follows C15 > C16 > C17 > C18. The higher yield of C15 in wet impregnated catalysts showed the major DCO_2 reaction. This was might be due to higher FFA value of RSO and comparatively lower surface area and limited amount of H_2 that led the reaction towards DCO/DCO_2. In contrast with sonochemical synthesized catalysts showed higher activity for C16/C18 hydrocarbons due to lower reduction temperature, small particle size, higher surface area, pore volume and pore size in addition with higher crystallinity (Ameen et al., 2016 a,b).
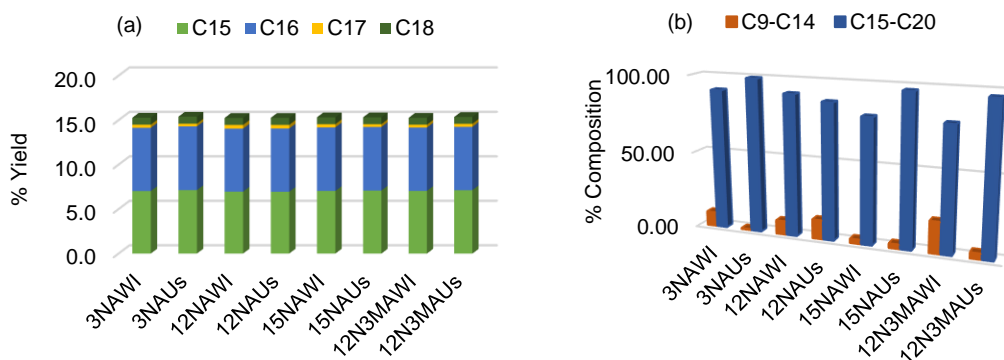

Figure 2: (a) Diesel range (C15-C18) hydrocarbons (b) total hydrocarbons composition of rubber seed oil over sonochemically synthesized and conventionally synthesized catalysts.

3.3. Triglycerides conversion

The time on stream with respect to conversion is shown in Figure 4. In the first hour of reaction, the hydrocarbon conversion was high in all catalysts except 3NAWI and 15NAWI. All sonochemically synthesized catalyst were active until 5 h with significant conversion more than 99 %. The conversion rate was constant for 3NAUs, 12NAWI, 12NAUs, 15NAUs, 12N3MAWI, and 12N3MAUs. 15NAWI catalyst conversion increased with respect to time but did not exceed more than 70 %. In the same way, 3NAWI also showed inconsistent behaviour for triglycerides conversion. In the first two hour, the conversion increased until 3 h time on stream in four and five-hour conversion increased however, did not exceed more than 62 %. The conversion of triglycerides and fatty acids into alcohols, aldehydes and other oxygenates as intermediates predicted the final product of respective

hydrocarbons. This constant behaviour of conventionally synthesized Ni/Al$_2$O$_3$ catalyst for conversion might relate with low metal loading, however, with similar metal loading sonochemically synthesized catalyst showed
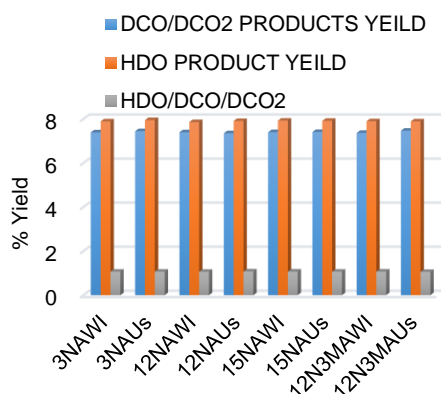

Figure 3: HDO/DCO/DCO$_2$ yield of rubber seed oil for diesel range (C15-C18) hydrocarbons over sonochemically synthesized and conventionally synthesized catalysts.
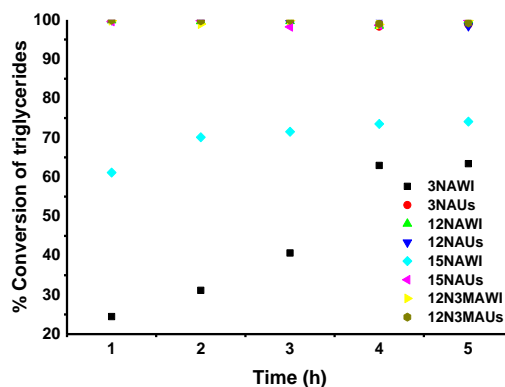
Figure 4: Triglycerides conversion on 5 h time on stream at 340 °C, 21 bar, WHSV=10, 150 H$_2$/oil ratios.

higher conversion up to 99.0 %. Harnos et al (Harnos et al., 2012) reported for hydrocarbon produced by sunflower oil over partly reduced 3 wt.% Ni/γ-Al$_2$O$_3$, non-sulfided catalyst. The catalyst was prepared wet impregnation method and tested for catalytic activity of sunflower oil in fixed bed tubular reactor at reaction condition of 340 °C, 21 bar, H$_2$: oil mole ratio 140, WHSV = 1-3 h^{-1}. The product yield for sunflower oil was reported C15 = 0.7 wt. %, C16 = 1.2 wt.%, C17 = 11.5 wt. % and C18= 1.1 wt. % and conversion 82.5 %. However, the almost similar composition, the 3 wt. % Ni/γ-Al$_2$O$_3$ (3NAUs) catalyst was synthesized using sonochemical method and treated with sunflower oil as bench mark. The sonochemical synthesized catalyst produced higher hydrocarbon i.e. C15 = 7.01 wt. %, C16 = 6.8 wt.%, C17 =0 .36 wt. % and C18 = 0.8 wt. % and higher conversion (99.95 %), significantly higher than reported by Harnos et al. (Harnos et al., 2012). The overall hydrocarbon produced in range of (C15-C18) reported by (Harnos et al., 2012) was (14.5 wt. %) whereas, sonochemically synthesized catalyst contributed higher yield (15.01 wt.%). Consequently, sonochemically-synthesized catalyst was determined significantly active for diesel range hydrocarbon and highly active for triglycerides conversion into hydrocarbons and other oxygenates. This lower hydrocarbon production may be restricted due to some operational conditions and equipment designed as well as also depends on feedstock composition as reported (Krár et al., 2010).

Conclusion

The utilization of ultrasound irradiation for the synthesis of Ni-Mo/Al$_2$O$_3$ type solid acid catalysts led to more active for hydrodeoxygenation of RSO compared to conventionally synthesized catalysts. Monometallic Ni/A$_2$O$_3$ synthesized via sonochemical method was 1.5 times more active than conventionally synthesized catalyst in terms of diesel range hydrocarbon yield (15.4 wt.%) and 1.7 times more active in terms of conversion (99.95 %). Similarly, the bimetallic Ni-Mo/Al$_2$O$_3$ sonochemically synthesized catalysts was more active for diesel range hydrocarbons and triglycerides conversion due to lower reduction temperature, homogenous dispersion of metal particles, higher surface area, higher pore volume and pore size as well as crystallinity increased that ultimately changed the shape of crystals that supported the higher activity of catalyst. The synthesis of nanocatalysts is also cost effective, the total cost of metal loading and energy consumption also reduced by the application of ultrasound-assisted method. In the production of hydrocarbon via hydrodeoxygenation, the sonochemically synthesized catalysts showed significant results in terms of % yield and % conversion in to value added compounds. The overall hydrocarbon yield in sonochemically synthesized was low compared to other feedstock such as Jatropha oil, sunflower oil, rapeseed oil due to limited H$_2$ supply, and low H$_2$: oil mole ratio as well as high WHSV nevertheless, significantly higher than conventionally synthesized catalyst. It is expected that with the variation in different reaction parameters, the hydrocarbon yield will be enhanced. The improvement in synthesis of solid acid catalysts via sonochemical method by variation in synthesis time, frequency, power can also enhance the catalytic activity for hydrodeoxygenation.

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