



Insitu upgradation of biocrude vapor generated from non-edible oil cake's hydrothermal conversion over aluminated mesoporous catalysts



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ABSTRACT

In this work, biocrude vapors generated from hydrothermal conversion of *Pongamia pinnata* cake using high pressure reactor at 400 °C and 25 kg/cm² were upgraded over three mesoporous catalyst namely SBA-15, KIT-6 and FDU-12. The catalysts were synthesized, aluminated and characterized using X-Ray Diffraction, N₂ adsorption-desorption, SEM techniques. A decrease in the surface area was observed on all three mesoporous catalyst after alumina loading with negligible effect on the pore diameter. Purely siliceous catalysts were found to give negligible effect on the yield of different product phases. Alumina supported SBA-15 (SAR 30) was observed as the suitable catalyst as compared to Al/FDU-12 (SAR 30) and Al/KIT-6 (SAR 30) for maximizing the biocrude yield with low heavy hydrocarbons (46.3 ± 2.2%), poly-aromatic hydrocarbons (17.1%) and acidic compounds (9.1%) content. Therefore series of SBA-15 were synthesized by varying silicon to alumina ratio between 20 and 50 for maximizing hydrocarbons with boiling cut fractions between 195 and 317 °C corresponding to gasoline range hydrocarbons. Al/SBA-15(SAR 40) was found to give highest biocrude yield (~34.8%) with highest selectivity towards gasoline fraction (23.7 ± 1.9%). GC/MS analysis was used to confirm the presence of aliphatic and aromatics. Highest asphaltene content was observed with Al/SBA-15 (SAR 50).

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1. Introduction

It is well known that globally, the energy demand is fulfilled by conventional fossil fuels available in nature [1]. Due to industrial growth and increase in life standard, energy demand has exponentially increased in last few decades creating serious issue of fuel crisis in the world. An increase of ~10% for the liquid fuel consumption has been observed in last 15 years. On above, the stringent environmental norms have forced governments, around the globe, for encouraging the use of new and renewable energy [2]. Particularly, biomass based fuel has been used in power sector as well as transportation sector and has undergone three generations, starting from use of edible/non-edible sources or lignocellulosic waste for biofuel production [3]. There is approximately four fold increase in the consumption of biofuel like ethanol and biodiesel since 2003 [4]. Conversion of various lignocellulosic biomass (agro,

industry, municipal, forestry) to biocrude has attracted the attention worldwide and are considered as a sustainable alternative for transportation sector. It is reported that if this waste is utilized properly, it can replace approximately 43% of the world petroleum consumption [5].

Jatropha curcusa and *Pongamia pinnata* has emerged as two major non-edible oil crops which are used to produce biodiesel by transesterification due to high (~30–40%) oil content [6,7]. At present the setup of large biorefineries or large biodiesel producing plants are still not a practical thought due to higher prices as compared to conventional fuel. However, in near future, to meet the 20% biodiesel blending policy, huge non-edible oil cake will be generated as solid waste which needs to be dispose-off properly and economically [8]. The edible oil cake has been used as cattle feed or manure but the cake obtained from non-edible oil cake is not suitable due to presence of few toxic compounds which could cause health issue. One of the suitable use of this seed cake can be its conversion to biofuel using pyrolysis [9,10]. It has been reported in literature that liquid fuel obtained from the pyrolysis of biomass has high viscosity, low calorific value and high content of

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oxygenated compounds like carbonyls (ketone and aldehydes), acids etc therefore these can't be used directly as engine fuel [11]. Further it is also reported that liquid fuel can be produced by providing high pressure condition in presence of water with biomass which gives higher biocrude yield with medium range hydrocarbons and low content of oxygenated compounds as compared to biocrude obtained from pyrolysis [12]. It is mentioned that high pressure (above atmosphere) and temperature (above 300 °C) creates a combination of aqueous phase reforming, subcritical water and steam exposure which favors in production of lighter compounds avoiding the formation of carbonaceous residue [13].

Upgradation of pyrovapors in presence of catalyst like ZSM-5, Co/MO_x, Ni/Mo_x, ZrO₂, SAPO are reported in literature [14]. ZSM-5, a widely used catalyst for biomass conversion studies, have tailorable acid strength and specific pore size. However, large size molecules of biocrude vapors face strong pore diffusion resistance inside the micropores of ZSM-5 and produce lesser liquid product. ZSM-5 also has ink-bottle type structure which results in higher coke yield [14].

Recently, the use of various mesoporous catalyst e.g. MCM-41, KIT-6, SBA-15, and FDU-12 have been reported in various industrial as well as biomass cracking reactions [15–19]. These catalysts are synthesized by using organic surfactant template with ionic and anionic properties. The pore diameter of these siliceous materials can be tailored between 5 and 50 nm making them favorable for mass transfer and diffusion of large molecules and provides easy access to active sites without any pore blockage [20,21]. Also due to their siliceous nature, mesoporous catalysts have electronically neutral framework with absence of acid sites. To increase their catalytic activity heteroatoms are incorporated by direct synthesis [22,23]. Since these materials do not have acid strength, alumina addition on SBA-15 and MCM-41 has been reported for cracking studies [24–26]. These active sites are Bronsted sites which help in the removal of oxygen from pyrovapors through carbonium ion mechanism through cracking, oligomerization, isomerization, cyclization, alkylation and aromatization etc. [27]. However, it is reported that the use of MCM-41 is not very promising at high pressure cracking due to its low hydrothermal and thermal stability [15,23,28].

In this study the effect of aluminated and non-aluminated mesoporous catalysts of varying pore size and structure was investigated on the yield and quality of biocrude obtained from hydrothermal pyrolysis of *Pongamia pinnata* seed cake.

2. Experimental

2.1. Biomass

Non-edible oil cake of *Pongamia pinnata* used in this work is obtained locally. The cake was first dried overnight in an oven at 110 °C. Organic templates used for the catalyst synthesis in this work (P123 and F127) were obtained from sigma Aldrich. Other chemicals used for analysis like KBr, CS₂, hexane, toluene, ethyl acetate, acetone were purchased from Agfa Acer and Fischer scientific.

2.2. Catalyst preparation

2.2.1. Synthesis of siliceous material

All three mesoporous catalyst were prepared using triblock copolymer P123 (for SBA-15 and KIT-6) and F127 (for FDU-12) as structure directing agent. P123 is known as poly(ethyleneoxide)-poly(propylene oxide)-poly(ethylene oxide) or EO₂₀PO₇₀EO₂₀ with avg molecular weight 5800 whereas F127 is known as

(poly(ethyleneoxide)-poly(propylene oxide)-poly(ethylene oxide)) or EO₁₀₆PO₇₀EO₁₀₆. All three siliceous materials were synthesized according to procedure reported in literature [28–31].

For synthesis of SBA-15 various materials added in the following molar ratio TEOS:P123:HCl:H₂O = 1:0.017:6:192 [28]. To start with Pluronic P123 (2 g) was mixed in water (15 g) and M HCl (60 g). To this solution TEOS (4.25 g) was added as source of silica with continuous stirring at 40 °C and maintained for 24 h under stirring conditions. The solution was then kept in an oven at 100 °C for 5 days under static and autogeneous pressure conditions.

High quality mesoporous 3D siliceous material FDU-12 was obtained as follow. The materials were added in the following molar ratio TEOS:F127:TMB:KCl:HCl:H₂O = 1:0.0037:0.5:3.36:6.08:165 [29]. In a beaker F127 (3 g) was added to 1.97 M HCl (185 mL). The mixture was maintained at 15 °C under continuous stirring. Further to this solution TMB (3.6 g) and KCl (15 g) were introduced, the solution was kept under stirring for 2 h and TEOS (12.5 g) was introduced to the mixture which was left at continuous stirring condition in an open container at 15 °C. The solution was then transferred to PP bottle, were closed tightly and placed in an oven at 100 °C for 5 days under autogeneous pressure condition.

For synthesis of KIT-6, following molar ratios were maintained: TEOS:P123:HCl:H₂O:BuOH = 1:0.017:1.83:195:1.31 [30]. In a typical batch, P-123 (6 g), water (217 g) and 35% HCl (11.8 g) was mixed in a beaker. Further 1-butanol (6 g) was poured into this solution with constant stirring at 35 °C. After 1 h stirring 12.9 g of TEOS was added drop wise at 35 °C. The beaker was kept under stirred conditions for 24 h at 35 °C. Thereafter the mixture was transferred to PP bottles and closed tightly for autogeneous pressure condition inside oven at 100 °C for 5 days.

After the hydrothermal treatment, three mesoporous catalysts were filtered and water washed, air-dried at 120 °C. The template of the three catalysts was removed by using ethanol extraction (twice) and were further calcined at calcined at 550° for 5 h [28–30].

2.2.2. Direct synthesis of aluminated catalyst

As the mesoporous catalysts are silica based catalyst, impregnation of acidic site via alumination is required to get favorable cracking results. Hence mesoporous catalysts were aluminated for experimental runs for SAR 30. Aluminum tri-sec-butylate was added to TEOS and HCl solution for 3 h at the beginning. The final product was separated using filtration which was further washed with distilled water and dried in an oven at 120 °C for 24 h. The mixture was then calcined at 500 °C for 5 h to get the final catalyst [31].

2.3. Experimental setup

Hydrothermal conversion followed by insitu upgradation was performed in a high pressure autoclave at pre-optimized process conditions: 400 °C, 25 kg/cm², reaction time: 35 min and W/B ratio of 2 (mass/mass) [32]. The autoclave consists of one Litre SS-316 vessel attached with magnetic agitator and coiled tube internal cooling system to control the temperature of the vessel. Pressure of the vessel was controlled by back pressure regulator (BPR). The reactor was filled with oil cake (50 g) and with water to biomass (W/B) ratio of 2:1 and catalyst to biomass (C/B) ratio of 1:10. Before feeding to the reactor, catalyst was sieved and only particle with diameter 0.2–0.5 mm were used for the experimental studies. Reactor vessel was then flushed with nitrogen and with the help of BPR the final pressure was fixed at 25 kg/cm². The reactor furnace heated to a temperature of 400 °C with a ramp rate of 20 °C min⁻¹. Outlet vapors from the vessel were passed through a horizontal shell and tube condenser and the final product was passed through

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