Fuel Processing Technology 119 (2014) 158–165

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Selective production of green gasoline by catalytic conversion of *Jatropha* oil

Sandeep K. Saxena, Nagabhatla Viswanadham *

Catalysis and Conversion Process Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India

ARTICLE INFO

Article history:
Received 16 July 2013
Received in revised form 15 October 2013
Accepted 5 November 2013
Available online 27 November 2013

Keywords:
Jatropha curcas oil
Strong acidity
Mesopores
Hydrogen transfer
Gasoline

ABSTRACT

A catalytic process for value addition of bio-oil derived from the *Jatropha curcas* plant through the production of green gasoline has been described. Four zeolite based catalysts possessing different porosity and acidity have been prepared by using Ultrastable Y (HY), Beta (BEA), micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5(NZ) zeolites. The textural properties of the samples have been characterized by XRD, SEM, BET surface area, pore volume, pore size distribution and micro-calorimetric ammonia adsorption studies. These catalysts have been exploited for the production of green fuel suitable for gasoline applications. Among the various catalysts, the nano-crystalline ZSM-5 synthesized in the laboratory exhibited excellent catalytic properties such as moderate acidity and stacking order of mesoporosity (which is absent in microcrystalline ZSM-5) responsible for the production of gasoline with as high as 77.4% selectivity and 95 research octane number (RON). The catalyst also exhibited enhanced time-on-stream stability supported by coke resistance ability (derived from TGA analysis of spent catalyst) when compared with the other zeolites within the studied period of 20 h. The present study provides a new catalytic process for production of gasoline from *J. curcas* oil for biorefinery.

1. Introduction

Fuel production from renewable feedstocks is continuously gaining importance and zeolite catalyzed processes are emerging as practical solutions for the effective conversion of these feedstocks through the production of hydrocarbons that belong to a wide range of fuels and chemicals [1,2]. The oils extracted from non-edible sources such as *Jatropha curcas* is one of the major feed sources for the economical way of production of fuels [3]. The ease in cultivation of the plant and its growth capacity in variety of dry and wastelands on one hand and its high oil content on the other hand qualify the plant as major alternative to the fossil fuel sources [4,5].

Among the various fuel types, the production of bio-diesel is widely studied by adopting trans-esterification reaction. However, the process requires long reaction times and consumes high quantity of methanol to produce mono-alkyl esters of long chain fatty acids [6,7]. The huge amount of glycerol (about 10%) obtained as unavoidable by-product during bio-diesel production also affects the product yields and process economics [8]. The bio-diesel obtained by this method also has some limitations to use alone for its practical applications of the fuel. In spite of its lower toxic emissions, the increased emissions of nitrogen oxides limit the use of pure biodiesel (B100) and not economical [9]. Therefore biodiesel requires fossil fuel as a blending-stock so as to make it suitable for use in diesel engine [10–12]. The blending of biodiesel is also limited by several factors, such as energy density, cold flow and stability. The higher the percentage of biodiesel blended (above 20%) the lower the energy content of diesel per gallon. High-level biodiesel blends can also impact engine warranties and formation of gel at cold temperatures and suffer from microbial contamination in tanks [9].

In addition, the pyrolysis process used for the bio-oil conversion needs high energy for facilitating high temperature reactions and produces mostly gaseous products along with diesel range straight chain hydrocarbons [13]. In search of efficient ways for value addition of *J. curcas* oil, production of relatively low boiling range hydrocarbon fuels such as gasoline through cracking based catalysis is gaining importance recently. The low temperature operation, controllable cracking reaction through tailored acid properties of the catalysts, low cost of production and ready to use quality of the gasoline product make this method practical for value addition of feedstock for industrial applications [14].

Zeolites possessing wide variation in porosity and tunable acidity have potential catalytic applications for a wide variety of molecular transformations, especially in hydrocarbon production not only from petroleum but also from the various types of renewable feedstocks such as *Jatropha* oil [15]. Among these, the ZSM-5 zeolite of pentasil family has advantage of shape selectivity suitable for formation of short range aromatics (benzene, toluene and xylenes) while avoiding the bulky molecular transformation leading to coke formation within the constraint space of pores advantageous for the life of the catalyst

---

* Corresponding author. Tel.: +91 135 2525856; fax: +91 135 2660202.
E-mail address: nvish@iip.res.in (N. Viswanadham).

0378-3820/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fuproc.2013.11.003

[16,17]. While the medium pore of ZSM-5 is suitable for the production of aromatics, the molecular size of triglycerides in the *Jatropha* oil suggests the need of larger pores for the effective transformation of the feed [18–20]. Acidity is another important property of the catalyst that influences the catalytic activity and the nature of the product.

Liu et al. produced C_{15}–C_{20} range hydrocarbon product from hydrotreatment of *Jatropha* oil over NiMoLa/Al_2O_3 catalyst [21]. While, Gong et al. applied NiMoP/Al_2O_3 catalysts for the production of high quality diesel blending stock (C_{15}–C_{18} range hydrocarbons) through hydro-treating of *Jatropha* oil [22]. Junming et al. have successfully produced high quality diesel range product from various woody oils (including *Jatropha* oil) using a variety of catalysts such as Al_2O_3, MCM-41 and CaO. Among these, the CaO catalyst is reported to exhibit the highest yield of (76 wt.%) organic liquid product along with 10 wt.% coke when using *J. Curcus* oil as feedstock [23]. Studies of Deng et al. indicated a superior performance of nanosized solid basic catalyst for the production of bio-diesel from *Jatropha* oil [24]. While most of these studies are concerned with bio-diesel production, very little is reported for the possible production of other carbon range products such as gasoline. The studies of Sharma et al. indicated the suitability of ZSM-5 catalyst for the conversion of *Jatropha* oil to produce gasoline along with kerosene and diesel range products [25]. Further studies by the same authors on micro-meso composite catalyst envision the need of additional mesoporosity for effective conversion of the *Jatropha* oil [26].

All the above-mentioned studies indicate the scope in catalyst development for the selective production of the desired hydrocarbon component. Since olefins are the intermediate species in the formation of aromatics and gasoline, the acidity of zeolites is expected to play vital role in the quality and yield of gasoline range product as in the case of fossil fuel processing. However, one cannot expect the similar product pattern in processing of fossil fuel and bio-oil (e.g. *Jatropha* oil) due to the difference in composition and complexity of the latter feed and thus initiates the need for studying the influence of such catalytic properties on the *Jatropha* oil conversion.

The oils extracted from non-edible sources such as *J. curcas* is one of the major feed sources for the economical way of production of fuels. The ease in cultivation of the plant and its growth capacity in variety of dry and wastelands on one hand and its high oil content on the other hand qualify the plant as major alternative to the fossil fuel sources. The value upgradation of such feedstocks viz. *Jatropha* oil through cracking is recently gaining importance due to its low temperature operation, controllable cracking reaction through tailored acid properties of the catalysts, low cost of production and ready to use quality of the gasoline product.

In an attempt to address the subject of selective production of gasoline from *J. curcas* oil and the influence of acidity and porosity properties of catalysts on the catalyst performance, we have conducted systematic studies on various catalysts that belong to micro-crystalline ZSM-5 (medium pore) (MZ), Beta (BEA) and Ultrastable Y (HY) (large pore) zeolites. In addition to this, a nano-crystalline ZSM-5 (NZ) exhibiting additional mesopores was also studied to understand the role of extra-porosity.

2. Experimental

2.1. Catalyst preparation

Micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5 (NZ) having Si/Al atomic ratio of 30 have been synthesized to understand the effect of acidity and porosity on *J. curcas* oil conversion. Another micro-crystalline zeolite sample HY (Si/Al atomic ratio 5) and BEA (Si/Al atomic ratio 25) are also used in the present studies. The properties of NZ exhibiting stacking order of mesoporosity is compared with the sample MZ.

2.1.1. Synthesis of micro-ZSM-5 (MZ) sample

In this synthesis, sodium silicate (Merck) was used as silica source and sodium hydroxide was slowly added to this solution, followed by the addition of aluminum nitrate and tetrapropyl ammonium hydroxide (TPAOH, Merck). The components were mixed with constant stirring at room temperature (25 °C). The pH of the resulting gel was then adjusted to 10.5 by adding 1:1 H_2SO_4 solution before charging it in Teflon lined autoclave for hydrothermal synthesis at 180 °C for 3 days (72 h) [27,28].

2.1.2. Synthesis of nano-ZSM-5(NZ) sample

In this synthesis tetraethyl orthosilicate (TEOS, Merck) was used as silica source. TEOS being an organic silica source was expected to come in the aqueous phase slowly. Al source was added slowly to precooled tetrapropyl ammonium hydroxide (TPAOH, Merck) solution and after that TEOS was added drop wise. The components were mixed with constant stirring. After adding all the ingredients, the solution was left to hydrolyze at room temperature (25 °C) for 41 h. The gel obtained was thus heated at 80 °C to evaporate water and ethanol formed during the hydrolysis of TEOS and to obtain a concentrated gel. The concentrated gel was charged in a Teflon lined autoclave for hydrothermal synthesis as in the case of MZ zeolite sample. The synthesis was performed at 170 °C for duration of 48 h [29].

All the synthesized samples were filtered and washed with deionized water, followed by drying at 100 °C and calcination at 500 °C for 4 h under vacuum. The powder forms of zeolites are converted into extrudates by mixing with 40 wt.% of pseudoboehmite powder followed by drying at 100 °C and calcination at 500 °C before using them for reaction [30,31].

2.1.3. Micro-crystalline BEA and HY catalysts

BEA zeolite with Si/Al atomic ratio 25 and HY zeolite with Si/Al atomic ratio 5 were obtained from Sud-Chemie India Ltd., in powder forms. These zeolite powders, MZ and NZ powders are shaped to extrudate form by mixing an inert alumina binder, pseudoboehmite with zeolite: binder ratio of 3:2 by weight, followed by adding sufficient amount of 3 vol.% glacial acetic acid for peptization. Wet extrusion of the resultant paste was carried out through a 2 mm in diameter size metallic syringe for the formation of wet extrudates. The extrudates were allowed to dry at room temperature overnight and further dried at 100 °C for 7 h followed by calcination at 500 °C for 4 h.

2.2. Physico-chemical characterization

The morphology and crystal structures of zeolties were characterized by the SEM (Quanta 200F instrument, Netherlands) and XRD (Rigaku Dmax III B, Japan). The N_2 adsorption–desorption isotherms were measured at 77 K on ASAP (Model 2010) Micrometrics USA instrument. Before measurement the samples were evacuated overnight at 250 °C. The BET surface area was calculated from linear part of plot according to IUPAC recommendations [32]. The micro-calorimetric measurement of ammonia adsorption was carried out at 175 °C. Differential heat of ammonia adsorption was determined by introducing small quantities of ammonia onto the outgassed sample, till the neutralization of all acid sites occurred on the catalyst surface. The heat of adsorption evolved for each dose was calculated from the resulting thermo-grams and the amount of ammonia adsorbed was calculated from the pressure change. Acidity of zeolite samples (extrudates) were measured from heats of adsorption of ammonia by micro-calorimetry. The amount of ammonia adsorbed per gram of catalyst was considered as the total acidity. The acidity is arbitrarily classified into (a) strong acidity (heat of adsorption > 100 kJ/mol), (b) medium acidity (heat of adsorption from 100 kJ/mol to 75 kJ/mol) and (c) weak acidity (heat of adsorption < 75 kJ/mol). The coke formed on the spent catalysts is evaluated by Thermogravimetric analysis (TGA, PerkinElmer Diamond). The thermograms of the samples are recorded between 298 and 1073 K with a heating rate of 10 °C/min at atmospheric pressure.

2.3. Catalyst evaluation studies

The feed *J. curcas* oil consists of C16:0 = 0.8, C16:1 = 18.2, C18:0 = 8.4, C18:1 = 47.8, C18:2 = 24.6 and C18:3 = 0.2 in wt.% (ACI Agro Solutions, Delhi) is processed in a fixed bed down flow reactor (220 mm length and 18.5 mm internal diameter) by loading 5.0 g of catalyst in the center of the reactor (schematic representation of microreactor unit is given in Fig. 1). Extrudates of α-alumina (inert material) were loaded above and below the catalyst bed. The feed *J. curcas* oil (without any dilution) was introduced into the reactor in a continuous flow using Eldex plunger type feed pump. While using N_2 as carrier gas the reaction is conducted at 550 °C reaction temperature, atmospheric pressure and 1.5 h^{-1} WHSV (weight hour space velocity). The product obtained at the end of the reactor was cooled with the help of a cold water circulator, where the entire product was separated into two products, namely, liquid product (collected from downstream) and gas product (collected through a gas bulb by water displacement method).

The gas product was analyzed using Varian capillary column, CP Al_2O_3/KCl (50 m × 0.53 mm × 10 μm) to give the analysis of C_1–C_5 hydrocarbons. Helium gas is used as carrier gas with 10 ml/min flow rate and the injector/detector temperature is 150/250 °C with oven temperature 190 °C. The gas product is analyzed by RGA (refinery gas analyzer) using Galaxie Varian software which provides the data with wt.% of components that include N_2, C_1, C_2, C_3, C_4 and C_5 hydrocarbons. The wt.% of C_1–C_5 (excluding N_2) is used for calculating the yields of individual gas components for mass balance in the final product. The liquid product was analyzed using Petrocal DH, 100% dimethyl polysiloxane as stationary phase (100 m × 0.25 mm × 0.5 μm). Helium gas is used as carrier gas with 2 ml/min flow rate and injector/detector temperature is 240/250 °C with oven temperature 230 °C. The American Standard Test Method (ASTM 6730) was used for detailed hydrocarbon group analysis, distribution of products and research octane number (RON) measure, where detailed hydrocarbon analysis (DHA) was obtained by using standard software Hydrocarbon Expert 4 (USA). The liquid product contained hydrocarbons ranging from C_5 to C_{12}. The performance of catalysts is evaluated based on their efficiency towards the conversion of tri-glycerides (in terms of oxygenate conversion), yield of liquid hydrocarbon product and the selectivity to gasoline.

$$\text{Conversion}(\%) = \frac{(\text{Mass of triglycerides (g) in the reactant}-\text{Mass of triglycerides (g) in the product})}{\text{Mass of triglycerides (g) in the reactant}} \times 100$$

$$\text{Yield of liquid hydrocarbon or gas (wt.\%)} = \frac{\text{Mass of liquid hydrocarbon (g) or gas (g) product}}{\text{Mass of feed (g)}}$$

$$\text{Gasoline selectivity (\%)} = \frac{\text{Mass of hydrocarbons in gasoline range (g)}}{\text{Mass of liquid product (g)}} \times 100$$

3. Results and discussion

The SEM images of the samples (Fig. 2) indicate the presence of nanometer range crystals in NZ while micrometer range crystals are observed in all other samples. The corresponding samples exhibited crystalline structure of BEA, Y and ZSM-5 zeolites in X-ray diffraction analysis (Fig. 3). Further, the low angle XRD patterns at about 0.3 2θ of NZ (inset of Fig. 3) exhibits typical (100) reflections that correspond to the mesopores. The N_2 adsorption–desorption isotherms (Fig. 4) of NZ indeed supported the presence of mesopores in this sample. Among the four samples, NZ exhibited the steep uptake of the gas at P/P0 of ~1.0 representing the well-defined mesopores, while that particular feature is absent in MZ having similar ZSM-5 structure. Table 1 contains the physico-chemical properties of the four catalysts used for the conversion of *J. curcas* oil. Among these, the HY catalyst exhibited

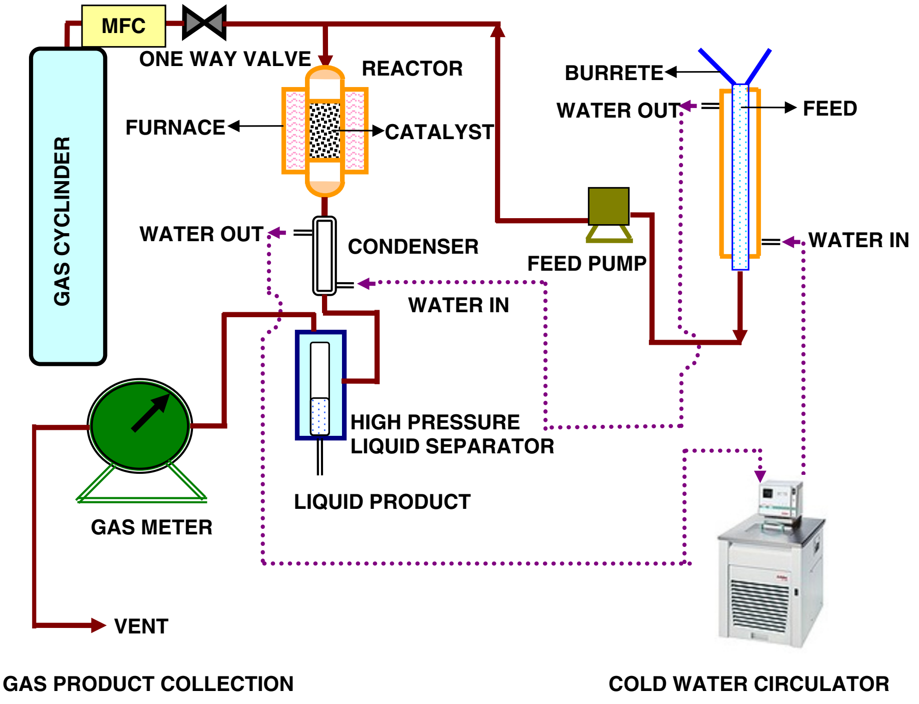

Fig. 1. Schematic representation of experimental setup for gasoline production from *Jatropha* oil.

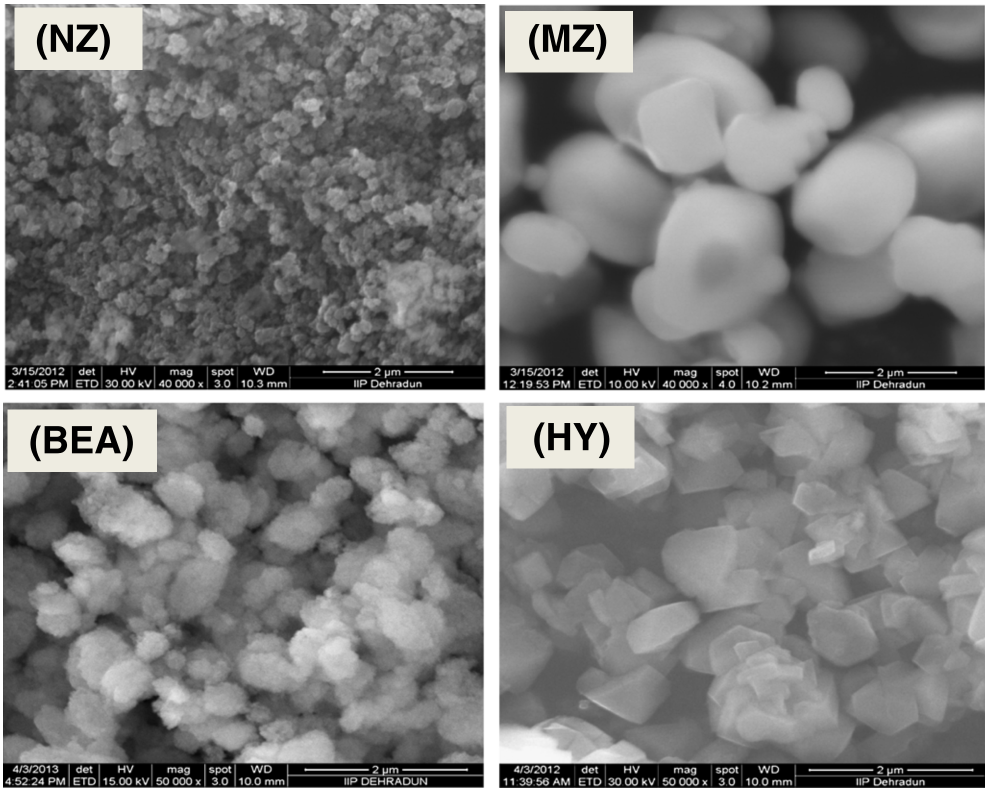

Fig. 2. SEM images of various zeolites.

highest surface area followed by BEA, NZ and MZ catalysts. The total pore volume of BEA is the highest, while those of HY and NZ are medium and comparable, with MZ being the lowest in terms of porosity. The acidity values of HY and BEA are comparable but higher than that of ZSM-5 catalysts (MZ and NZ). The two ZSM-5 catalysts exhibit comparable acidity as expected from their similar Si/Al atomic ratio of 30.

The *J. curcas* oil containing oxygenates is processed over the four acidic catalysts in the present study. The higher C/H ratio of the feed composition is expected to give olefinic intermediates, where the attempts are made in the present study to divert these olefins towards aromatization reaction for the selective production of gasoline range hydrocarbons. The reaction performance of catalysts given in Table 2 indicates that all the catalysts exhibited almost 100% conversion of *J. curcas* oil (in terms of oxygenate conversion) at the reaction conditions studied, where, various product components obtained in gas and liquid hydrocarbon forms are summarized for comparison purpose. The liquid hydrocarbon product contains major amount of aromatics followed by olefins, isoparaffins, paraffins and naphthenes, whereas the gas contains C_1 to C_4 hydrocarbons and hydrogen, CO_2 and CO. The yield of gas product ranges from 28 to 41 wt.% on various catalysts and the composition of which comprises C_2–C_4 olefins, C_1–C_4 paraffins, CO, CO_2 and a small amount of hydrogen. The liquid hydrocarbon product is always high with 52.8 to 69.1 wt.% that consists of major amount of aromatics (28 to 45.5 wt.%) followed by small amounts of paraffins, isoparaffins, olefins, naphthenes and unidentified product. The high amount of aromatics in the liquid product reflected in the higher research octane number (RON 65 to 95) of the hydrocarbon pool. Performance comparison of four catalysts given in Table 2 indicates that the order of gas yields increases from NZ < MZ < BEA < HY, while the reversible trend is observed in liquid hydrocarbon yields HY < BEA < MZ < NZ. It is interesting to see that the trend in gas yields is following the catalytic property of acidity (Table 1), which means the higher crackability of the molecules on strong acid sites is the reason for the higher gas yields on HY and BEA when compared to those on ZSM-5 based catalysts (MZ and NZ). Among these, the NZ catalyst gives highest liquid hydrocarbon yield and gasoline selectivity with research octane number (RON) of 94.6 (Fig. 5) suitable for gasoline blending applications.

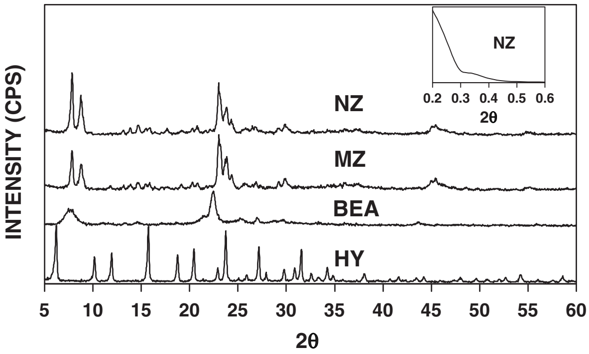

Fig. 3. XRD patterns of various zeolites.

3.1. Trends in paraffin formation

The paraffin yields and the distribution of individual paraffin components are observed to be different on the various zeolite catalysts (Table 2). Among the various paraffins, propane is predominant on MZ (9.6 wt.%) and NZ (12.3 wt.%) catalysts, while C_1 paraffin is high on BEA and C_2 paraffin is high on HY catalyst. The higher amounts of

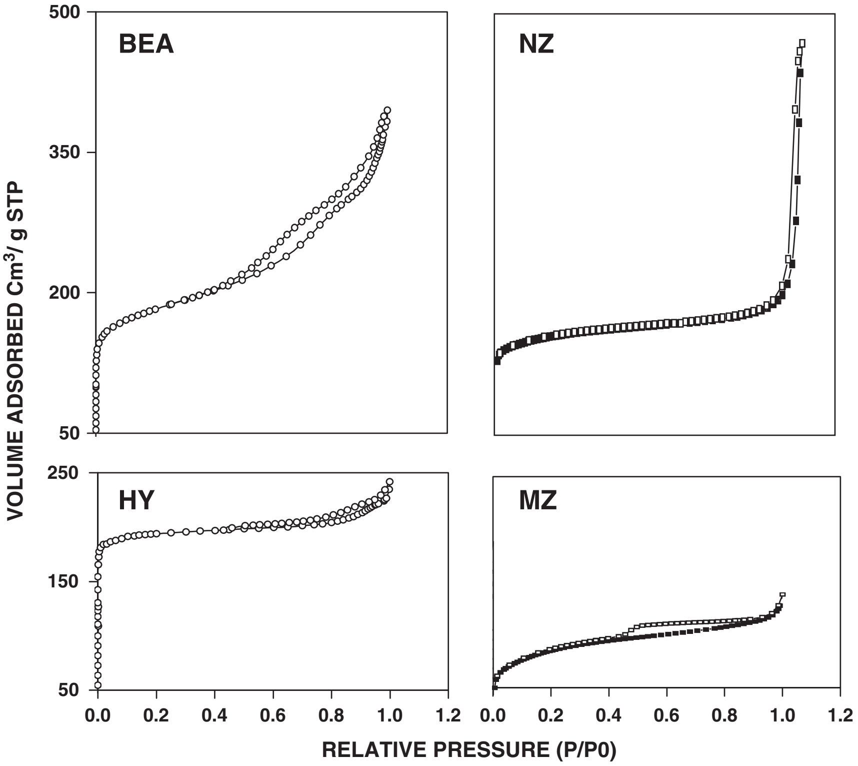

Fig. 4. Nitrogen adsorption–desorption isotherms of zeolites.

C_1,C_2 on HY and BEA may be due to their higher intrinsic acidic property (Table 1), where the low acidity ZSM-5 catalysts (NZ and MZ) encourage the formation of C_3 rather than C_1,C_2.

3.2. Trends in olefin formation

Among the various catalysts, MZ catalyst exhibited the highest olefin yield followed by HY, BEA and NZ (Table 2). While C_5+ olefins are comparable on all the catalysts, the C_2 to C_4 olefins are in very low amount on the NZ catalyst. But, the aromatic yields are high on NZ catalyst (Table 2). This clearly indicates the effective conversion of C_2 to C_4 olefins facilitated on NZ catalyst to yield higher aromatic product.

3.3. Trends in aromatic distribution

Among the four catalysts, the NZ exhibited the highest aromatic yield of 45.5 wt.%, while the aromatic yield on other three catalysts are low (~28 wt.%) and comparable. The higher liquid hydrocarbon yield with higher aromatic content results in as high as 77.4% selectivity to gasoline on the NZ catalyst. The NZ catalyst also exhibited the aromatic product rich in toluene and xylenes, with low amounts of C_9+ aromatics and benzene along with resultant research octane number (RON) of 95, which is advantageous for gasoline applications. However, the product obtained on all other catalysts (HY, BEA and MZ) exhibits inferior quality in terms of aromatic selectivity and composition due to the presence of considerable amounts of benzene and C_9+ aromatics and lower RON of 65 to 78.

Table 1
Physico-chemical properties of various zeolite based catalysts.

Properties	MZ	NZ	BEA	HY
BET surface area (m^2/g)	342.4	465.4	514.8	825.5
External surface Area (m^2/g)	90.4	139.4	193.4	81.7
Micropore area (m^2/g)	256.8	323.4	321.5	770.9
Total pore volume (cm^3/g)	0.1773	0.3815	0.6111	0.3386
Micropore volume (cm^3/g)	0.1022	0.1301	0.1688	0.2640
Mesopore volume (cm^3/g)	0.0751	0.2514	0.4423	0.0746
Acidity* (mmol·NH_3/g)	0.79	0.80	0.88	0.92
Strong	0.18	0.08	0.40	0.48
Medium	0.42	0.32	0.28	0.32
Weak	0.19	0.40	0.20	0.12

* Acidity is determined by micro-calorimetric studies.

3.4. Factors responsible for better performance of NZ

The NZ catalyst exhibiting low amount of C_1,C_2 paraffins when compared with BEA and HY zeolite based catalysts indicates the lower cracking severity of the catalyst manifested by the presence of low acidity of the ZSM-5 catalyst. However, in spite of having similar acidity, the MZ catalyst exhibits different product patterns from that of NZ, especially in terms of olefins and aromatics. Table 2 reveals that the product obtained on NZ catalyst contains low amount of C_2 to C_4 olefins and higher olefins along with higher yields of aromatics when compared with the corresponding MZ catalyst. This can be explained by the reaction pathways given in Fig. 6, where the lower olefins (C_2 to C_4) formed from *J. curcas* oil through the dehydration, de-carbonylation, decarboxylation and cracking reaction act as source for the formation of higher olefins that eventually undergo cyclization and dehydrogenation reactions to yield aromatics. Here the olefins act as source for the formation of cyclic intermediates as well as hydrogen acceptors from the resultant cyclic intermediates. However, the formation of aromatics requires the final step of hydrogen transfer (HT) from cyclic intermediates to olefins, which is a bulky bi-molecular reaction (Fig. 6). Since, both the NZ and MZ catalysts exhibit comparable acidity, the presence of mesopores in NZ may be responsible for the

Table 2
Product composition and catalyst performance.

Catalysts	HY	BEA	MZ	NZ
Conversion	100.0	99.7	96.2	100.0
Product yields (wt.%)				
(I) Gas yield	40.2	39.3	29.4	28.3
C_1	1.6	7.3	2.5	3.6
C_2	10.1	3.8	2.2	2.8
C_2^{I}	4.1	4.0	4.1	1.4
C_3	4.7	3.0	9.5	12.3
C_3^{I}	7.1	5.1	4.5	1.2
iC_4	0.4	0.3	0.9	0.7
C_4	1.6	0.4	0.6	0.3
C_4^{I}	4.1	2.9	2.3	0.3
H_2	1.2	4.9	1.9	2.6
CO_2	3.1	1.8	–	0.7
CO	2.2	5.8	0.9	2.4
(II) Liquid yield	58.2	60.0	70.1	71.6
Paraffins	3.1	5.1	3.9	2.8
C_5	0.4	0.5	0.4	0.1
C_6	0.3	0.8	0.6	0.3
C_7	0.6	1.6	0.8	0.6
C_8	0.3	0.4	0.4	0.3
C_9	0.2	0.3	0.2	0.2
C_{10}–C_{17}	1.3	1.5	1.5	1.3
Isoparaffins	3.6	3.3	5.0	3.0
C_5	0.2	0.2	0.3	0.1
C_6	0.1	0.1	–	0.1
C_7	0.2	0.2	0.3	0.2
C_8	0.8	0.4	1.5	0.9
C_9	0.1	0.1	0.5	0.2
C_{10}	1.0	1.1	0.9	0.5
C_{11}	0.9	1.0	1.1	0.9
C_{12}^{+}	0.3	0.2	0.4	0.1
Olefins	9.2	7.4	15.8	11.2
C_5	3.3	2.6	3.3	1.7
C_6	2.7	2.6	3.7	3.6
C_7	1.6	1.4	2.9	2.1
C_8	0.4	0.2	1.9	0.7
C_9	–	0.3	0.3	0.1
C_{10}–C_{17}	1.2	0.3	3.7	3.0
Naphthenes	2.5	2.0	3.6	2.9
C_5	0.2	0.1	0.2	0.1
C_6	0.3	0.2	0.4	0.2
C_7	0.4	0.4	0.4	0.1
C_8	0.7	0.6	0.7	1.1
C_9	0.8	0.4	1.5	0.9
C_{10}	0.1	0.1	0.4	0.2
C_{11}^{+}	–	0.2	–	0.3
Aromatics	28.0	27.6	28.1	45.4
C_6	5.2	4.1	4.1	3.0
C_7	6.6	6.6	7.4	16.8
C_8	5.1	5.7	7.1	17.0
C_9	2.6	2.7	2.9	3.1
C_{10}	4.5	4.5	3.8	2.8
C_{11}	3.5	3.6	2.3	2.2
C_{12}	0.5	0.4	0.5	0.6
Unidentified hydrocarbons with oxygenates	6.4	11.4	5.8	3.7
(III) H_2O	5.4	3.2	7.9	2.5
(IV) Coke	1.6	0.7	0.5	0.1
Total (I + II + III + IV)	100.0	100.0	100.0	100.0
RON	65.1	67.9	78.0	94.6

Reaction conditions: T = 550 °C, N_2 gas flow = 12 L/h, WHSV = 1.5 h^{-1}.

enhanced aromatization activity required for facilitating bulky bimolecular hydrogen transfer reactions. The decrease in olefins with simultaneous increase in aromatics observed in the product over NZ when compared with MZ (Table 2) indeed supports the enhanced HT activity of this catalyst. Furthermore, the absence of mesopores in MZ encouraged the conversion of C_5+ olefins to propene through cracking rather than their conversion to aromatics.

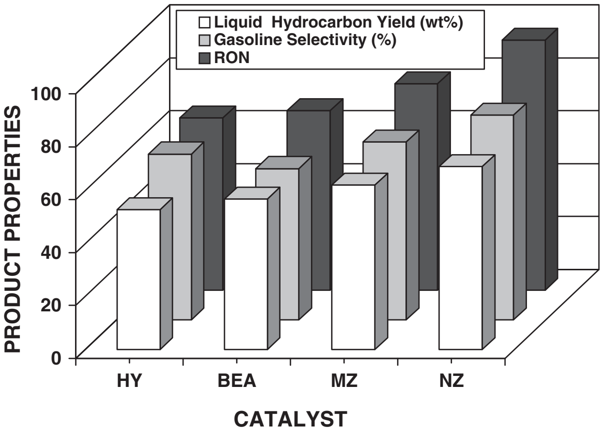

Fig. 5. Performance of various catalysts in gasoline production from *Jatropha* oil.

The NZ catalyst also exhibited enhanced time-on-stream (TOS) activity when compared with other catalysts (Fig. 7A). The TGA analysis of spent catalysts shown in Fig. 7B further indicates the superior performance of NZ in terms of coke resistance. It is known that the coke precursors deposited in the pores of the molecular sieves are mostly hydrogen deficit organic molecules that burn at higher reaction temperatures (>400 °C) when compared with those formed on the outer surface (200 °C) (saturated hydrocarbons) [33]. The cumulative value of the weight loss occurred above 200 °C is taken for estimating the coke formed on the various catalysts in the present study, where the formation of coke is observed to be the lowest on NZ catalyst (1.9%) followed by MZ (9.4%), BEA (14.7%) and HY (32.1%). The low coke formation in ZSM-5 catalysts (MZ and NZ) is understood from the space constraint in medium size pores for the formation of bulky coke precursors. In addition to this, the presence of mesopores in NZ seems to play a vital role by providing facile diffusion of the olefins and aromatics that further minimizes the formation of bulky coke precursors on NZ catalyst. The reaction temperature influenced the liquid hydrocarbon yield as well as gasoline selectivity and both the values are increased with reaction temperature up to 550 °C (Fig. 8A). This trend is due to the enhanced occurrence of endothermic aromatization reaction at higher reaction temperatures. However, above this temperature (>550 °C) the liquid hydrocarbon yield decreased while that of gaseous product increased that suggests the enhanced occurrence of cracking reactions at higher reaction temperature (Fig. 8A). The enhanced cracking reaction

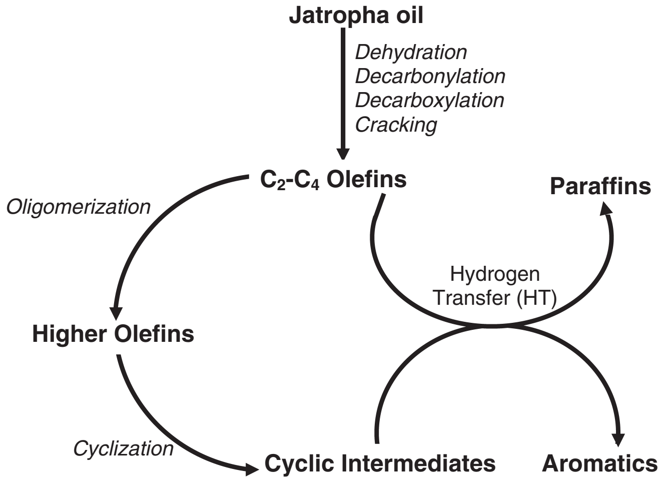

Fig. 6. Reaction pathways for the formation of aromatics from *Jatropha* oil.

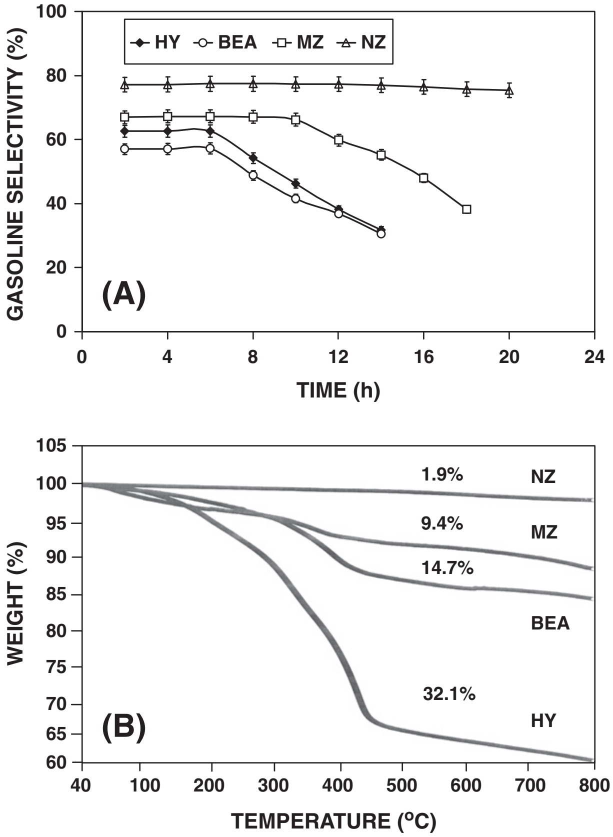

Fig. 7. (A) Time-on-stream performance of the catalysts (reaction conditions: T = 550 °C, N_2 gas flow = 12 L/h, WHSV = 1.5 h^{-1}). (B) TGA analysis of the corresponding spent catalysts.

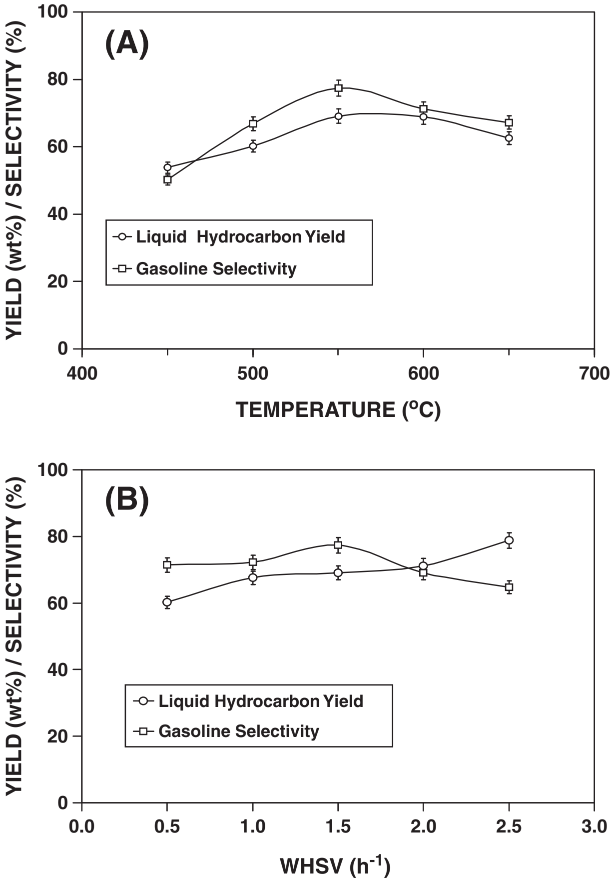

Fig. 8. Performance of NZ catalyst at (A) various reaction temperatures and (B) feed WHSV.

occurred at higher reaction temperatures reflected in the decrease in selectivity to gasoline range (C_5 to C_9) hydrocarbons with simultaneous increase in the C_1 to C_4 hydrocarbons.

Similarly the feed WHSV (weight hourly space velocity) of 1.5 h^{-1} was observed to be optimum for achieving higher liquid hydrocarbon yields and gasoline selectivity (Fig. 8B). The liquid yield as well as gasoline selectivity increased up to the WHSV of 1.5 h^{-1}. Though the increase in liquid yield is continued with further increase of the WHSV above 1.5 h^{-1}, the selectivity to gasoline is decreased above this value. In other words, the optimum balance between liquid yield and gasoline selectivity is observed at the WHSV of 1.5 h^{-1}, where the contact time of reactant on the catalyst seems to be optimum to minimize the cracking reaction and for the formation of aromatics (Fig. 8B).

Overall, the better performance of NZ when compared to MZ is ascribed to the presence of moderate acidity and higher mesopore volume (Table 1). Furthermore, the inferior performance of BEA and HY samples when compared with NZ clearly indicates the presence of strong acidity in these samples responsible for higher cracking activity (Table 1). Here NZ stands as the best catalyst among the four samples by virtue of its moderate acidity (with less strong acidity and more medium acidity) for the production of high quality gasoline, whose properties are comparable with that of the petroleum gasoline (Table 3). Furthermore, with high aromatic content, high octane, low olefins and zero sulfur (Table 3), it could be a good gasoline blending stock to mix with variety of low octane feed stocks such as naphtha for fuel applications.

4. Conclusions

Various zeolite based catalysts exhibiting different acidity and porosity properties have been explored for the conversion of *J. curcas* oil into gasoline range hydrocarbons. The lower acidity with medium size pores possessed by ZSM-5 makes advantage for the production of higher liquid hydrocarbon yields (~69 wt.%) and octane number (~95) suitable for gasoline applications. The presence of additional mesopores in NZ (compared with MZ) facilitated enhanced bulky bimolecular hydrogen transfer reactions responsible for the higher aromatic yields on one hand and enhanced time-on-stream stability on the other hand that makes the catalyst suitable for effective value upgradation of the *J. curcas* oil.

Acknowledgments

The authors are thankful to director of IIP-CSIR for his encouragement and SKS thanks the director for approving his Ph.D. studies. We acknowledge the catalyst characterization and product analysis groups at IIP for their support.

Table 3
Fuel properties of gasoline and *Jatropha* oil conversion product.

Properties	Gasoline	*Jatropha* oil conversion product
Octane number	91	94.6
Density at 15 °C (kg/cm^3)	710–770	720–760
IBP (°C)	35	37
FBP (°C)	210	215
Sulfur (wt.%)	0.005	nil
RVP (kPa) at 38 °C	60	64
Aromatics (vol.%)	42	63.4 (wt.%)
Olefins (vol.%)	21	15.6 (wt.%)

References

[1] J.C. Serrano-Ruiz, R.M. West, J.A. Dumesic, Catalytic conversion of renewable biomass resources to fuels and chemicals, The Annual Review of Chemical and Biomolecular Engineering 1 (2010) 79–100.

[2] G.W. Huber, S. Iborra, A. Croma, Synthesis of transportation fuels from biomass: chemistry, catalysts and engineering, Chemical Reviews 106 (2006) 4044–4098.

[3] T.V. Rao, G.P. Rao, K.H.C. Reddy, Experimental investigation of Pongamia, *Jatropha*, Neem methyl esters as bio-diesel on C.I. engine, Jordan Journal of Mechanical and Industrial Engineering 2 (2008) 117–122.

[4] A.B. Chhetri, M.S. Tango, S.M. Budge, K.C. Watts, R.M. Islam, Non edible plant oil as new sources for biodiesel production, International Journal of Molecular Sciences 9 (2008) 169–180.

[5] D. Vashist, M. Ahmad, A comparative study of castor and *Jatropha* oil sources and its methyl ester test on the diesel engine, International Journal of Engineering, Science and Technology 3 (2011) 4765–4773.

[6] A. Sivasamy, K.Y. Cheah, P. Fornasiero, F. Kemausuor, S. Zinoviev, S. Miertus, Catalytic Applications in the Production of Biodiesel from Vegetable Oils, ChemSusChem 2 (2009) 278–300.

[7] J.V. Gerpen, Biodiesel processing and production, Fuel Processing Technology 86 (2005) 1097–1107.

[8] C.H. Zhou, J.N. Beltramini, F.Y.X.Y. Xian, G.Q. Lu, Chemo-selective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals, Chemical Society Reviews 37 (2008) 527–549.

[9] M. Kousoulidoua, L. Ntziachristos, G. Fontaras, G. Martini, P. Dilara, Z. Samaras, Impact of biodiesel application at various blending ratios on passenger cars of different fueling technologies, Fuel 98 (2012) 88–94.

[10] K. Bozbas, Biodiesel as an alternative motor fuel: production and policies in the European union, Renewable and Sustainable Energy Reviews 12 (2008) 542–552.

[11] F. Ma, M.A. Hanna, Biodiesel production a review, Bioresource Technology 70 (1999) 1–15.

[12] F. Billaud, V. Dominguez, P. Broutin, C. Busson, Production of hydrocarbons by pyrolysis of methyl esters from rapeseed oil, Journal of the American Oil Chemists' Society 72 (1995) 1149–1154.

[13] W. Xiong, X. Li, J. Xiang, Q. Wu, High density fermentation of microalga chlorella protothecoides in bioreactor for micro bio-diesel production, Applied Microbiology and Biotechnology 78 (2008) 29–36.

[14] G. Ramya, R. Sudhakar, J.A.I. Joice, R. Ramakrishnan, T. Sivakumar, Liquid hydrocarbon fuels from *Jatropha* oil through catalytic cracking technology using AlMCM-41/ZSM-5 composite catalysts, Applied Catalysis A: General 433 (2012) 170–178.

[15] C. Zhao, J.A. Lercher, Upgrading pyrolysis oil over Ni/HZSM-5 by cascade reaction, Angewandte Chemie International Edition 51 (2012) 5935–5940.

[16] A. Croma, G.W. Huber, L. Sauvanaud, P. O'Connor, Processing biomass derived oxygenates in the oil refinery: catalytic cracking reaction pathways and role of catalyst, Journal of Catalysis 247 (2007) 307–327.

[17] T. Dickerson, J. Soria, Catalysis fast pyrolysis: a review, Energies 6 (2013) 514–538.

[18] J.D. Adjaye, N.N. Bakhshi, Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: comparative catalyst performance and reaction pathways, Fuel Processing Technology 45 (1995) 185–202.

[19] T.Y. Leng, A.R. Mohamed, S. Bhatia, Catalytic conversion of palm oil to fuels and chemicals, Canadian Journal of Chemical Engineering 77 (1999) 156–162.

[20] T.L. Chew, S. Bhatia, Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery, Bioresource Technology 99 (2008) 7911–7922.

[21] J. Liu, C. Liu, G. Zhou, S. Shen, L. Rong, Hydrotreatment of *Jatropha* oil over NiMoLa/Al_2O_3 catalyst, Green Chemistry 14 (2012) 2499–2505.

[22] S. Gong, A. Shinozaki, M. Shi, E.W. Qian, Hydrotreating of *Jatropha* oil over alumina based catalyst, Energy and Fuels 26 (2012) 2394–2399.

[23] X. Junming, J. Jianchun, C. Jie, S. Yunjuan, Biofuel production from catalytic cracking of woody oils, Bioresource Technology 101 (2010) 5586–5591.

[24] X. Deng, Z. Fang, Y.H. Liu, C.L. Yu, Production of bio-diesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst, Energy 36 (2011) 777–784.

[25] R.K. Sharma, M. Anand, B.S. Rana, R. Kumar, S.A. Farooqui, M.G. Sibi, A.K. Sinha, *Jatropha* oil conversion to liquid hydrocarbon fuels using mesoporous titanosilicate supported sulfide catalysts, Catalysis Today 198 (2012) 314–320.

[26] F.A. Twaiq, A.R. Mohamed, S. Bhatia, Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicate mesoporous catalyst with various Si/Al ratios, Microporous and Mesoporous Materials 64 (2003) 95–107.

[27] R.J. Argauer, G.R. Landolt, Crystalline zeolite ZSM-5 and method of preparing the same, US Patent (1972) 3702886.

[28] N. Viswanadham, S.K. Saxena, J. Kumar, P. Sreenivasulu, D. Nandan, Catalytic performance of nano crystalline H-ZSM-5 in ethanol to gasoline (ETG) reaction, Fuel 95 (2012) 298–304.

[29] M. Singh, R. Kamble, N. Viswanadham, Effect of crystal size on physico-chemical properties of ZSM-5, Catalysis Letters 120 (2008) 288–293.

[30] V. Grieken, J.L. Sotelo, J.M. Menendez, J.A. Melero, Anomalous crystallization mechanism in the synthesis of nanocrystalline ZSM-5, Microporous and Mesoporous Materials 39 (2000) 135–147.

[31] N. Viswanadham, R. Kamble, M. Singh, M. Kumar, G. Muralidhar, Catalytic properties of nano-sized ZSM-5 aggregates, Catalysis Today 141 (2009) 182–186.

[32] K.S.W. Sing, D.H. Everett, T. Sieminiewiska, Reporting physico-sorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure and Applied Chemistry 57 (1985) 603–619.

[33] X. Guo, Y. Zheng, B. Zhang, J. Chen, Analysis of coke precursor on catalyst and study on regeneration of catalyst in upgrading of bio-oil, Biomass and Bioenergy 33 (2009) 1469–1473.