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Production of renewable aviation fuel range alkanes from algae oil

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1   **Production of renewable aviation fuel range alkanes from algae oil**

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6   **Abstract**

7   Jet fuels produced from sources other than petroleum are receiving considerable attention since

8   they offer the potential to diversify energy supplies while mitigating the net environmental

9   impact of aviation. Here we report a novel single-step catalytic process for the production of jet

10   fuel range alkanes from a renewable oil source, algae oil. The catalyst materials were

11   characterized using scanning electron microscopy, X-ray diffraction, surface area and pore size

12   measurements. The feedstock and the product hydrocarbons were characterized using gas

13   chromatography. We discuss the effect of temperature, pressure, time, catalyst type and quantity

14   on feedstock cracking quality and selectivity. The results show that Ce exchanged zeolite β

15   shows higher selectivity towards C10-C14 hydrocarbons at elevated temperatures and pressures.

16   A high liquid product mass conversion of 98% was obtained at a temperature and reaction

17   pressure of 400 °C and 400 psi, respectively. Selectivity was 85% for cracking algae oil on 4%

18   Ce exchanged zeolite β and thus the catalyst shows promise for the synthesis of aviation range

19   hydrocarbons for future large scale bio-jet fuel production.

20   *Keywords*: Jet fuel; Hydrocarbons; Zeolite β; Biofuel;

21

1   **Introduction**

2   The fear of depleting our fossil fuel reserves and the concern about the impact on the

3   environment stemming from the use of fossil fuels have led to a growing interest in using

4   renewable feedstock as alternative fuels[1]. Vegetable oils have attracted interest as feedstock for

5   the past few decades[2, 3]. The annual production of oils and fats for generating biofuels could be

6   increased without diverting farmland for energy production[4]. Non-edible, high oil content crops,

7   waste vegetable oils and fats are being used nowadays to reduce the raw material cost and to

8   reduce the use of edible oils to produce alternative transportation fuels[5]. Apart from land-based

9   second generation crops, billions of dollars are invested in an attempt to develop biofuels from

10   high-lipid microalgae grown in photobioreactors[6]. These have low productivity, so growth of

11   non-specific algal biomass could be a favored approach to provide the annual tonnage of biomass

12   needed for fuel production[7]. Ocean based biomass such as phytoplankton, waste from shellfish[7]

13   and finfish processing[8], becomes an important supplement feedstock to the bio-refinery[9]. So, the

14   large scale production of marine macroalgae using an ocean-based cultivation system could be a

15   potential solution for the use of algae on a large scale for renewable fuel production[10].

16

17   Traditionally, hydrocarbons fractions for aviation fuel are produced from fossil fuel sources[11].

18   However, recent studies have shown that they can also be obtained from the catalytic and

19   thermal cracking of alternative renewable oil sources[12, 13]. Such studies include treating oils at

20   higher temperatures (350−550 °C) with various cracking catalysts. Cracking processes are

21   widely used in the chemical industry to convert heavy oil fractions into lighter liquid

22   hydrocarbons (C5 to C15)[14, 15]. Cracking can be accomplished using several methods each

1   leading to its own characteristic product composition. Catalytic cracking operates at relatively

2   milder conditions than non-catalytic cracking processes[16].

3   Under specific process conditions, these alternate oil sources have a strong potential for the

4   production of liquid fuels which meet fuel specifications, such as gasoline, diesel and aviation

5   fuel[17, 18]. In addition, the gas fraction is also rich in various hydrocarbons in the C2-C4 range[19].

6   Vegetable oils have been hydrotreated to produce straight-chain alkanes are constituents of jet or

7   diesel fuels[20]. Palm oil was converted catalytically into an organic liquid product (OLP) at 450

8   °C in a micro-activity unit (MAT unit) over microporous HZSM-5 zeolites, mesoporous MCM-

9   41 zeolites, and composite mixtures of these two. Depending on the catalyst type, conversions in

10   the range of 77 to 99 wt% have been obtained[21]. In the catalytic cracking of canola oil, relatively

11   high concentrations of aromatics, predominantly consisting of benzene, toluene, and xylenes,

12   were found in the OLP (~ 95 wt%). Also, the formation of water as a by-product was observed[22].

13   But some studies suggest that a catalyst may not even be essential for forming a product with a

14   relatively high amounts of aromatics[23].

15   Studies on the thermochemical conversion of biomass have shown that hydrocarbons in the

16   gasoline range were predominant in the liquid product whereas the gaseous fraction contained

17   both paraffinic and olefinic hydrocarbons[24]. Feedstock conversion and the type of products

18   obtained have been shown to depend strongly on operating conditions, such as reaction

19   temperature, space velocity, and the type of feedstock. Furthermore, catalysts possess different

20   characteristics that could affect product distribution, such as strength or density of acid sites,

21   surface area, crystallinity, and shape selectivity[24-26]. The specific role of each of these

22   characteristics on feedstock conversion is still debated[27]. For example, some studies suggest that

23   a catalyst with higher acid strength will lead to greater feedstock conversion and a higher amount

1 of aromatic hydrocarbons in the product fraction[28, 29]. However, these results were in

2 contradiction to the findings of other workers who showed that the formation of aromatic

3 hydrocarbons or any other type of hydrocarbons does not necessarily require the presence of acid

4 centers on the catalyst[30, 31]. Table 1 summarizes reaction conditions and the different types of

5 catalysts used in hydrocarbon synthesis.

6 Zeolites, also referred to as molecular sieves, offer an advantage in that they enable the catalysis

7 of certain reactions depending upon compositional and structural characteristics, while

8 preventing other reactions. This makes the process very specific. On the other hand, a high

9 reaction specificity could be a disadvantage if the zeolite is not perfectly tailored or formed [32]. It

10 is synthesized in the presence of an organic template, tetraethylammonium hydroxide[33]. Zeolite β

11 has been widely used in industrial processes such as cracking[34], petroleum refining, fine

12 chemical synthesis,[35-37] and inorganic chemical conversion[38]. Zeolite β possesses unique three-

13 dimensional network of large pores (12MR) and exhibits excellent acidic catalytic properties[39].

14 Zeolite β crystallites are rough and have a diameter of ~50 nm[40]. Predominantly, catalyst acidity

15 has been modified principally by incorporating metal cations or by changing the silica/alumina

16 ratio[41-43].

17 Cerium(III) is known to be a strong base compared to the trivalent lanthanides[44], and gallium is

18 amphoteric (acts as an acid or a base, depending on the reaction conditions)[45]. Thus, in the

19 present work, zeolitic catalysts were prepared by exchanging Ce^{3+} and Ga^{3+}onto zeolite β. Ce-Ni

20 catalyst (a well-known hydrotreating catalyst) was also prepared by incipient wetness

21 impregnation to act as a comparative control. The conversion of algae oil and palmitic acid to

22 hydrocarbons was studied over these catalysts and their performance was evaluated. We also

23 determined the optimum reaction variables to maximize the production of jet fuel range

1   hydrocarbons. To the best of our knowledge, and as reported in a fairly recent review[46], very few

2   studies have focused on the synthesis of diesel fuel fractions and aviation fuel fractions (HEFA

3   jet) from algae oil[47]. That used a multi-step, multi-catalyst process (deoxygenation, selective

4   cracking and isomerization)[47]. This study proposes a single-step, single-catalyst process to

5   achieve the same.

6

7

8   **Experimental**

9   All chemicals and reagents were purchased from Sigma-Aldrich and were of analytical grade or

10   better. The chemicals were used without further purification. Zeolite β was prepared using a two-

11   step hydrothermal synthesis. First, a solution was prepared by dissolving 59.13 g of silicic acid

12   (89% SiO_2) in 202.2 g of 40 wt% tetraethylammonium hydroxide in water. This was added to a

13   second solution containing 1.48 g of Al-pellets and 2.69 g of sodium hydroxide (98.9%) in 17.7

14   g of water. The two solutions were mixed to form a reaction mixture with the composition

15   (expressed in mole ratios of oxides):

16   $1.2\ Na_2O\text{-}10.0(TEA)_2O\text{-}Al_2O_3\text{-}32.0\ SiO_2\text{-}306.2\ H_2O$

17   This reaction mixture was placed in a 0.3 L Teflon lined steel autoclave and heated to 150 °C for

18   6 days. This resulted in a large amount of crystalline material. The product was separated from

19   the mother liquor and washed with distilled water. It was filtered and dried overnight in an oven

20   at 100 °C. 10 g of the synthesized zeolite β was suspended in 250 mL of cerium

21   hydroxide/gallium chloride aqueous solution (0.2M), and then the mixture was vigorously stirred

1 at room temperature for 3 hours. The Ce or Ga/zeolite β was then washed with deionized water,

2 filtered and dried at 100 °C for 2 hours. Nickel nitrate hexahydrate and cerium nitrate

3 hexahydrate were dissolved in deionized water prior to the addition of zeolite β. This mixture

4 was continuously stirred at room temperature for 24 hours and then dried at 120 °C for 12 hours.

5 Finally, all samples were calcined for 4 hours in an electrical furnace maintained at 450 °C. Prior

6 to reaction, the catalysts were reduced at 550°C for 6 h in a flow of hydrogen and nitrogen.

7 The algae oil cracking was performed over the synthesized catalysts at pressure ranging from

8 150 psi to 400 psi, temperature ranging from 200 to 360 °C, and reaction times ranging from 1 to

9 4 hours. The calcined catalyst was used in crushed powder form to minimize mass-transfer

10 effects and reactions used the catalysts at an amount of 1.5 wt% of the feedstock. A mixture of

11 tetradecane/dodecane and the catalyst was initially added to the feedstock and the stainless steel

12 autoclave reactor was heated to the desired reaction temperature under a mixture of

13 helium/hydrogen gas flow at a constant rate maintaining the required pressure. After a certain

14 period, the products were allowed to cool to room temperature. The catalyst was allowed to settle

15 down and was separated from the products. The liquid product was distilled. The distillate

16 fraction was the organic liquid product (OLP), which was analyzed, and the amount of residual

17 oil was weighed after each experiment. Table 2 shows the independent factors (X_i), levels and

18 overall experimental design of the most significant experiments.

19 X-ray diffraction patterns were obtained with a Rigaku Smartlab 3kW X-ray diffractometer using

20 CuKα radiation. The scan step size was 0.02 degrees and the scan speed was 0.5 degrees per

21 minute. Nitrogen adsorption and desorption isotherms were measured at 77 K using a

22 Micromeritics ASAP 2010 system. The samples were degassed for 10 h at 300 °C before the

23 measurements. Scanning electron microscopy images were collected using a Hitachi S-4700

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1   electron microscopes. Jet fuel samples were analyzed with an Agilent 7890A gas chromatograph

2   (GC) equipped with a 30 m × 0.25 mm × 0.33 μm HP-5 capillary column and a flame ionization

3   detector. A 1 μL sample was injected into the GC with a split ratio of 100:1, and the carrier gas

4   (nitrogen) flow rate was 11 mL/min. The temperatures of the injector and detector were 280 °C

5   and 300 °C, respectively. The oven temperature program consisted of a 4 min soak at 40 °C

6   followed by a 10 °C/min ramp up to 280 °C, which was held for 5 min.

7   **Results**

8   The catalyst obtained at the end of the reaction consisted of white spherical particles. Zeolite β

9   particle size was ~0.36 microns. The particle size[48] and the spherical shape of the particles

10 formed were similar to those reported previously[49-51]. Figure 1a shows the zeolite β framework

11 and Figure 1b shows the cerium exchanged framework. There was no significant change in the

12 shape and size of the particles after the exchange of Ce ions.

13 Figure 2 shows XRD patterns of calcined zeolite β spheres. The sample contained a very small

14 amount of amorphous material and exhibited high crystallinity. The X-ray diffraction (XRD)

15 pattern of calcined zeolite β shows well-resolved peaks in the 5–40° range, that are characteristic

16 of the zeolite β structure. Small peaks between 2θ =5–10°and 20–30° confirm the formation of

17 zeolite β[33]. XRD spectra (Fig. 2) were compared with those of the Peak Information Software,

18 PDXL 2 and were found to be in agreement with those of aluminum silicate, ceria and aluminum

19 cerium.

20 Figure 3a shows a cumulative volume distribution with respect to pore diameters. It is apparent

21 that the bulk of the pores fall within a diameter range of about 100 Å to about 1000 Å. These

22 pore characteristics are influenced both by the molecular characteristics of the zeolite and by the

1 metal exchange method. Interestingly, N_2 adsorption/desorption isotherms (Fig. 3b) of calcined

2 catalyst exhibit a step at a relative pressure, P/P_0, of 0.8–0.95, as a result of the presence of

3 mesostructures. The small difference in adsorption between the branches of the hysteresis loop

4 suggests that mesopores make a small contribution to the amount adsorbed. However, the sample

5 exhibits a high degree of structural ordering as inferred from steepness of the capillary

6 condensation step on the adsorption isotherm.

7 The surface area of the highly crystalline zeolite β spheres was determined to be ~640 m^2g^{-1}. The

8 surface area depends upon the silica/alumina ratio and the surface area observed was comparable

9 to previously reported values[52].

10 Following distillation, the samples were analyzed with a gas chromatograph. The reaction

11 products were identified by their fragmentation patterns. Fragmentation patterns were

12 determined by matching gas chromatograph retention times with known standards.

13 Quantification of the main product components was performed using calibration curves for each

14 compound of interest. Straight chain (or normal) alkanes, branched alkanes, cyclic alkanes or

15 cycloparaffins, and aromatic alkanes (aromatics) were found in the product. Under these pressure

16 and temperature conditions, lighter hydrocarbons such as CH_4 and C_2H_6 occur as gases, while

17 hydrocarbons larger than pentane are found as liquid or solid. We observed a very small amount

18 of coke residue.

19 Figure 4 shows the gas chromatograph obtained from one of the reaction products. The fraction

20 contains n-alkanes with carbon chains possessing fewer than 14 carbon atoms, together with

21 several other unsaturated and/or cyclic hydrocarbons whose peaks appear at retention times

22 between 2 and 12 minutes. No peaks were recorded after 14 min for such samples. It is probable

1   that aromatic hydrocarbons, such as benzene, toluene and xylene, are also volatilized to some

2   extent since they have higher vapor pressures than 14 carbon n-alkanes. Some samples also

3   contained saturated aliphatic hydrocarbons with carbon chain lengths greater than 17 carbons and

4   methyl esters at retention times greater than 15 minutes. Figure 5 shows the gas chromatograph

5   obtained from one such sample. In general, from the data above, the branched alkanes are closer

6   together and the corresponding straight-chain alkanes boil at higher temperature. Thus, branched

7   alkanes elute first, followed by the straight-chain alkanes.

8   **Discussion**

9   Studies relating to one-step processes in which a catalytic material catalyzes isomerization and

10   cracking are scarce. Only a few reports have appeared in the literature, most of which are on the

11   production of green diesel[53, 54]. A few examples of reports that have studied different oil sources,

12   reaction conditions, catalysts, and main products of hydrocracking vegetable oils are listed in

13   Table 1.

14   Jet fuel or aviation fuel (Jet-A, Jet A-1, and JP-8) is a distillate fraction that consists of a mixture

15   of straight and branched alkanes, aromatics, and cycloalkanes. C10 to C14 hydrocarbons are

16   typical. Petroleum-derived jet fuels usually contain ~20% aromatics, but an ideal jet fuel would

17   have lower aromatic content. However, aromatics in the fuel are essential to prevent the seals

18   from shrinking and to avoid fuel leaks. Our experimental results have demonstrated the

19   technological feasibility of obtaining high yields of jet fuel range alkanes from algae oil which

20   are supported by some important observations.

21   It has been observed that the solvent to feedstock ratio should be higher than 2:1 to maximize

22   hydrocarbon yield. Cerium exchanged zeolite β was found to be the most effective catalyst to

1   generate a product containing hydrocarbon compounds in the jet fuel range. Also, the catalyst

2   quantity required was less than 1.5 wt% of oil used in the reaction. Previous research has

3   demonstrated that catalysts which provide relatively low (alpha values of between 0.600 and

4   0.700) to moderate (alpha values of between 0.700 and 0.800) chain growth probabilities tend to

5   provide high yields of light (C2-C7) alpha olefins[55]. Examples of such catalysts include co-

6   precipitated iron-cobalt catalysts, titania, mixtures of titania and alumina, and supported

7   ruthenium catalysts[56-59]. In comparison, use of Ce exchanged zeolite β led to the formation of

8   products containing significant portion of relatively high molecular weight (C7-C14) and low

9   molecular weight fractions (C2-C7). Since fraction composition may vary, some routine

10   experimentation was necessary to identify the optimal process conditions and to determine the

11   effectiveness of the catalyst in the production of jet fuel range hydrocarbons. Decane solvent

12   mixture and algae feedstock oil were subjected to cracking. Plain solvent mix did not produce

13   fuel. Feedstock oil by itself did not produce lower chain C compounds either; however there was

14   a change in the spectra between the feedstock and the treated oil.

15   The overall liquid product was weighed and a mass conversion obtained at the end of 4 hours of

16   reaction at 250 °C was ~50%. Therefore, it was hypothesized that higher conversion could be

17   obtained by further optimizing the reaction system. Over recent decades these processes have

18   been very challenging due to undesired decomposition and polymerization reactions at high

19   temperatures[60, 61]. In general, olefin conversion by cracking increases with increasing pressure

20   and temperature. Thus, the optimal pressure for carrying out the process needs to be determined.

21   A 93% conversion was previously observed in the cracking of algae oil on Pt/US-Y zeolite

22   bifunctional hydrocracking catalyst at 350 °C and 800 psi[47]. In this study, to form more straight

23   chain alkanes and lower alkenes, the H_2 pressure required was higher than 200 psi. A pressure of

1   250 psi yielded higher fractions of n-alkanes and lower aromatics content. Temperatures lower

2   than 200 °C did not convert oil efficiently; the product remained viscous after reaction

3   completion. The conversion of oil to gasoline and jet fuel range hydrocarbons increased with

4   prolonged reaction time, and increased continuously with increasing reaction temperature in the

5   range of 250 to 360 °C. Above 400 °C, selectivity for x-decanes were relatively lower than those

6   at lower temperatures and by-products such as alkenes were detected in higher amounts.

7   Table 3 lists the hydrocarbons identified in the jet fuel samples. It was found that zeolite β was

8   highly selective for formation of hydrocarbons in the jet fuel boiling range. Figures 6a-d show

9   the hydrocarbon selectivity obtained at various reaction conditions. Maximum jet range

10   hydrocarbon yield was about ~71% at reaction conditions of 300 °C and 400 psi over 4 hours

11   (Fig. 6a), while the maximum yield reached ~85% when the reaction was conducted at 400 °C

12   and 400 psi for 6 hours. Further, the selectivity at different temperatures for the Ce/zeolite β

13   support increases rapidly with reaction temperature and reaches a high value at 300 °C at which

14   an unexpectedly high C10-C14 selectivity is obtained. Selectivity towards C10-C14

15   hydrocarbons was the highest at a reaction pressure of 250 psi and remained almost constant

16   thereafter (Fig. 6b). Similarly, the reaction time was optimized at 6 hours (Fig. 6c). The overall

17   selectivity for the individual C5-C18 hydrocarbons when different catalysts were used was also

18   compared. Different patterns are observed for all three catalysts (Fig. 6d). It is interesting to note

19   that for both the catalysts, the maximum selectivity was observed for C6-C14 alkanes among

20   hydrocracked components (C5-C18).

21   In a recent project, bifunctional catalysts NiMo/HY carbide and nitride catalysts were used for

22   hydrocracking of vegetable oils to jet fuel range components. Around 2 g of the catalyst at a

23   reactor pressure of 650 psi and temperature range of 360-450 °C produced 16-20 wt% of jet fuel

1 and a 20-29 wt% of diesel range hydrocarbons[62]. Also, when used cooking oil was used as a

2 feedstock, at reaction conditions of 390 °C and 2000 psig, 81.88 % conversion was obtained with

3 a 20% selectivity towards the formation of kerosene/jet range hydrocarbons[63]. Cracking

4 composition and selectivity can also vary due to feedstock composition. For example, microalgal

5 species such as Rhodophyta, possess <30% in C18 carbons. So, the cracking products would

6 differ greatly depending on the species of algae used. This has been reviewed in detail by Yang

7 et al, where the carbon distributions of lipids in different types of algae and characteristics of jet

8 fuels derived from algae by four pathways has been discussed thoroughly[64]. A recent study

9 employed sulfided Ni–Mo catalyst supported on high surface area semicrystalline ZSM-5, the

10 algal triglyceride conversion reached a maximum (99%) at 430 °C while the yield of jet-fuel

11 range product reached a maximum selectivity (77%) at 410 °C[65]. Similar tests on *J. curcas* oil

12 have shown that it is possible to obtain a liquid biofuel with yields greater than 80 wt.%

13 composed mostly of hydrocarbons, around 83% of which the majority are C8–C18, using

14 decarboxylation, which is a process that has lower yields than hydrodeoxygenation[66].

15 The process reported here, although operates in a similar temperature range, has more selectivity

16 towards jet fuel range hydrocarbons at a pressure below 400 psi.

17 Hydrodeoxygenation (as shown in equation 1) yields an organic liquid product (OLP), together

18 with gaseous products and water[67].

19 $Triglycerides \xrightarrow{H_2} Propane + R_1CH_3 + R_2CH_3 + R_3CH_3 + 6H_2O$

20 ...(1)
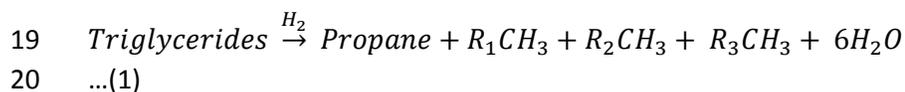
21 Following thermal breakdown and oxygen removal of the triglyceride molecule, the heavy

22 hydrocarbon compounds are then cracked into paraffins and olefins as a result of thermal and

23 catalytic mechanisms[68]. During the process, an n-alkane can be hydroisomerized with some

1   degree of branching; which can be described as illustrated in Figure 7, if only considering methyl

2   group branches for simplification[69].

3   The reaction includes the hydrogenation of the C=C bonds of the oils followed by oxygen

4   removal to produce alkanes. This can occur through three different pathways: decarbonylation,

5   decarboxylation and deoxygenation[67]. Since both decarbonylation and decarboxylation remove

6   one carbon atom from the fatty acid chain, the yield will be lower when compared to

7   deoxygenation. So, deoxygenation is preferred[64]. Deoxygenation of oils, by itself, produces an n-

8   paraffin product ranging from nC15-nC22, which is a product in the diesel fuel range but too

9   heavy for jet fuel range[70]. On the other hand, the hydrodeoxygenation system, used in the current

10   study utilizes a site-specific target catalyst which employs selective hydrocracking of the n-

11   paraffin product along with substantial isomerization to produce jet fuel range hydrocarbons. The

12   selective cracking and isomerization could be either simultaneous or sequential.

13   The reaction pressure, temperature and amount of solvent were optimized and the optimized

14   conditions were found to be 6 hours at 400 °C, 400 psi, using 0.1 g of catalyst and tetradecane, 5

15   g/dodecane, 5 g for 10 g of feedstock charged. The total mass conversion obtained under these

16   conditions was ~98%.

17   The experimental data was then fit to a first order polynomial equation given below.

18   **Conversion % = $1.89 \cdot 10^{-1}$* temperature + $2.67 \cdot 10^{-1}$* pressure + 15.6 * time - 85.74**   …(2)

19   The analysis of variance (ANOVA) indicated that the model (Eq. (2)) was significant and

20   adequate to represent the relationship between the response (percent weight conversion) and the

21   significant variables, with very small p-value (0.03) and a satisfactory coefficient of

22   determination (R^2=0.83). There was no main effect for solvent quantity with an *F*-value of 4.51,

1   which is too low and a *P*-value of 0.38, which is greater than 0.05. Since the catalyst quantity

2   used was very low, it did not have a prominent effect, however, there is a small interaction

3   between catalyst quantity and solvent quantity with an *F*-value of 2.13 and a *P*-value of 0.49.

4   The selectivity of the catalysts towards the formation of C6-C9, C10-C14, C15-C18 alkanes and

5   aromatics, esters and FFA remaining in the products is given in Figure 8a-b. It can be seen that

6   experiment 8 was the most significant with the least amount of aromatics and the highest

7   selectivity towards the formation of jet fuel range fraction. Thus, the reaction conditions

8   associated with experiment 8 to be the optimal conditions for the production of aviation fuel

9   range hydrocarbons.

10   During the last decade, there has been increasing interest in producing renewable green liquid

11   fuels from hydroprocessing various non-conventional lipid feedstocks, and this work is a step

12   towards developing a technology that could be commercialized. This study is aimed at

13   developing catalysts to form bio-derived jet fuel from renewable resources, and more

14   particularly, for use as alternatives or additives to petroleum-based or gas-to-liquid produced

15   products.

16   **Conclusion**

17   This paper demonstrates the conversion of algae oil to jet fuel range hydrocarbons. The catalyst

18   type plays a significant role in the reaction process. Ce/zeolite β catalyst was used at the fixed

19   conditions of T = 400 °C, H_2/He gas mix at P of 400 psi, reaction time 6 hours, 0.1 g of catalyst

20   and 10 g of feedstock. C10-C14 alkanes was found to comprise over 85% of the product and an

21   overall liquid product mass conversion of ~98% was obtained. The products from this single-step

22   process meet the basic requirements for jet fuel range boiling hydrocarbons. The synthesized

1   catalyst also exhibited better product yields. Green fuels, at present, are not a substitute for fossil

2   fuels, due to limited resources and high temperature and pressure requirements to produce them.

3   But by making only a few process modifications, they can be used as drop-in additives to their

4   corresponding fossil fuels.

5   **Acknowledgements**

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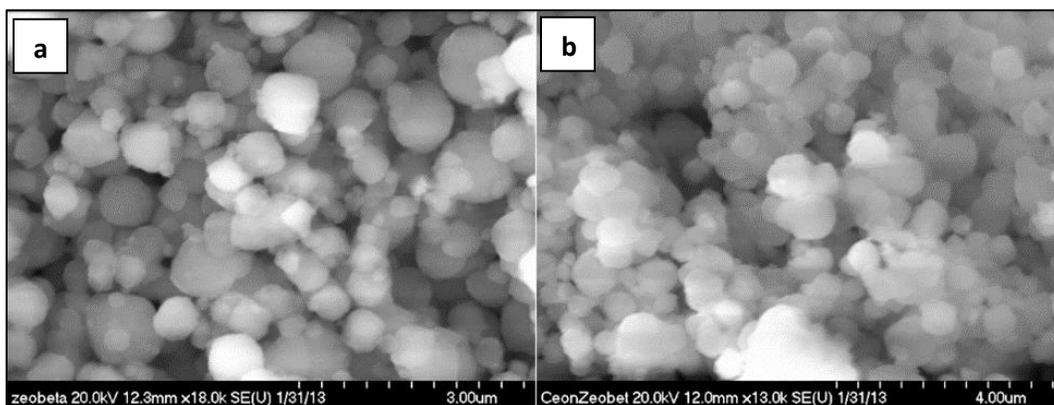
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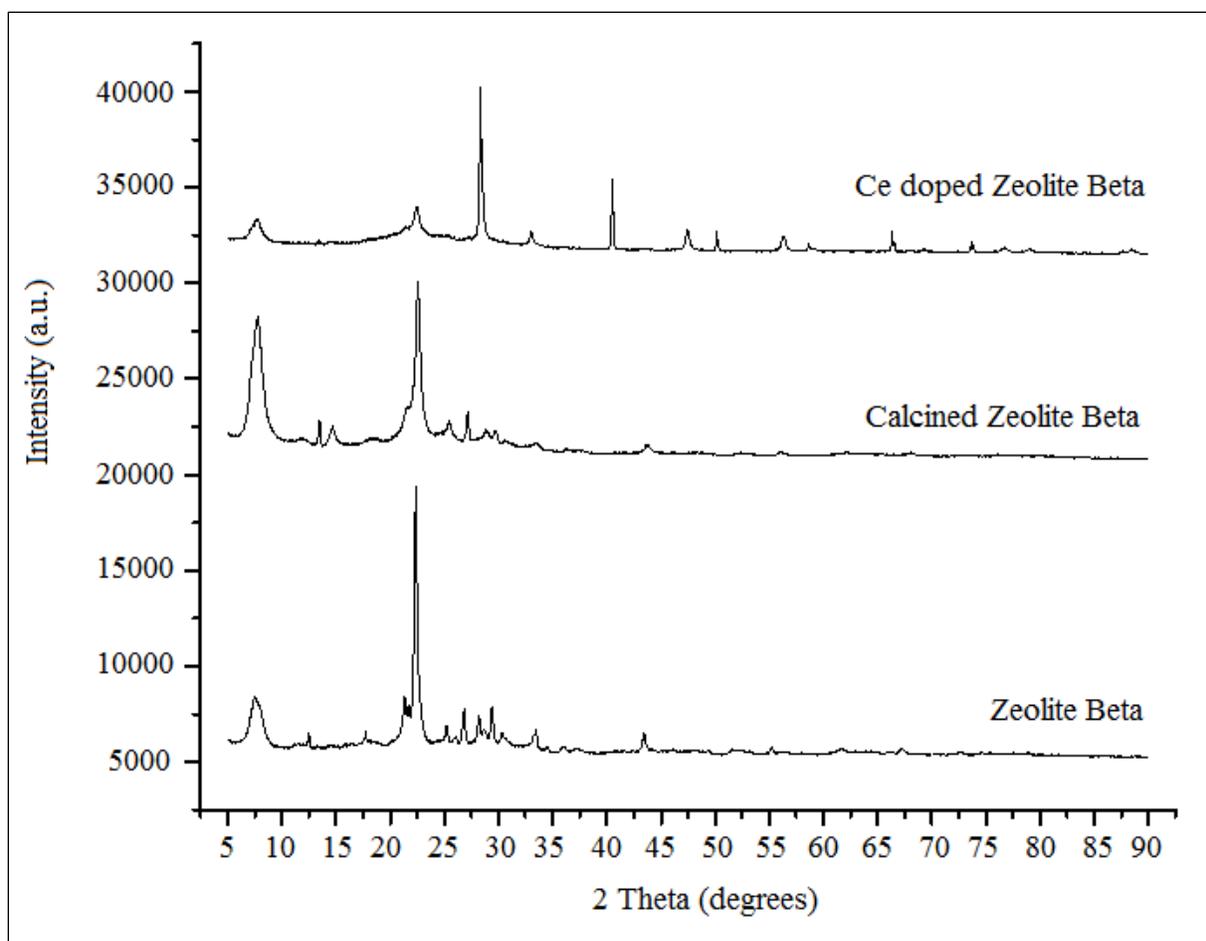
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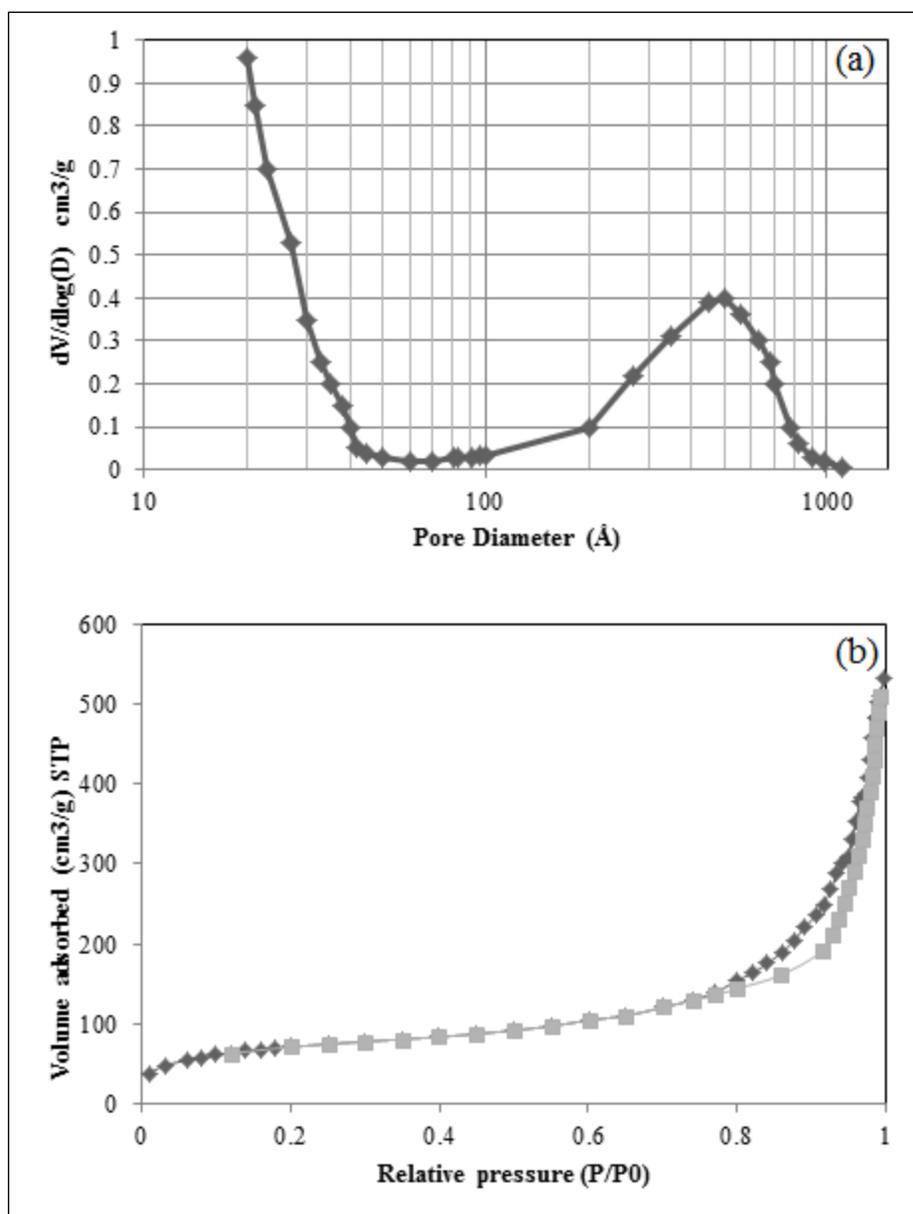
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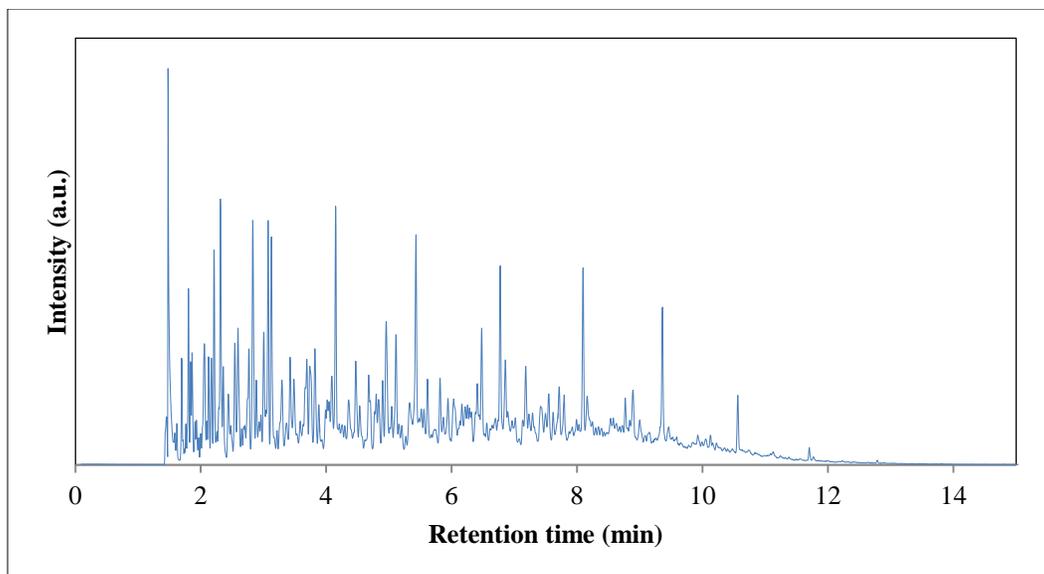
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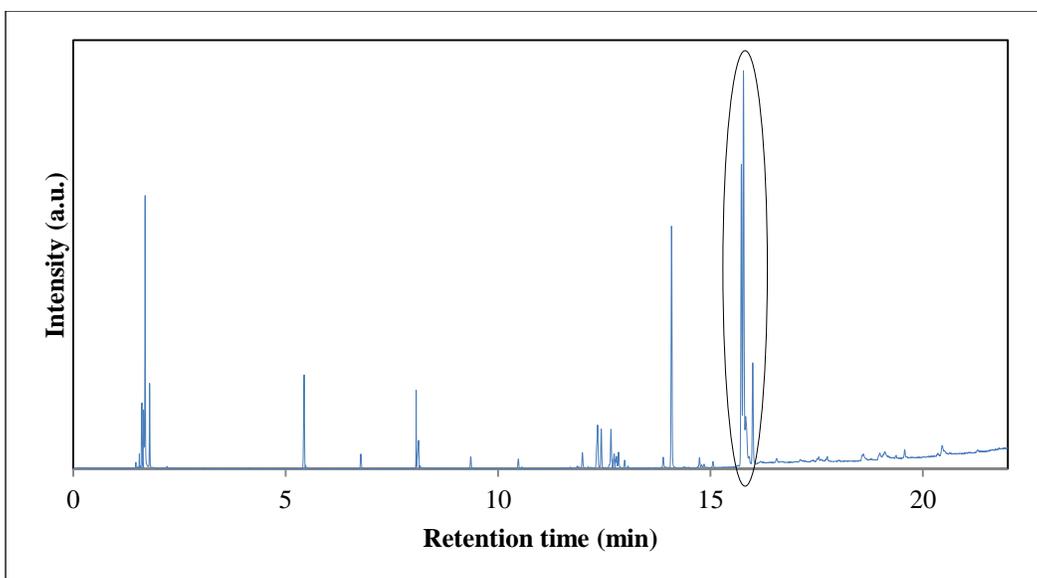
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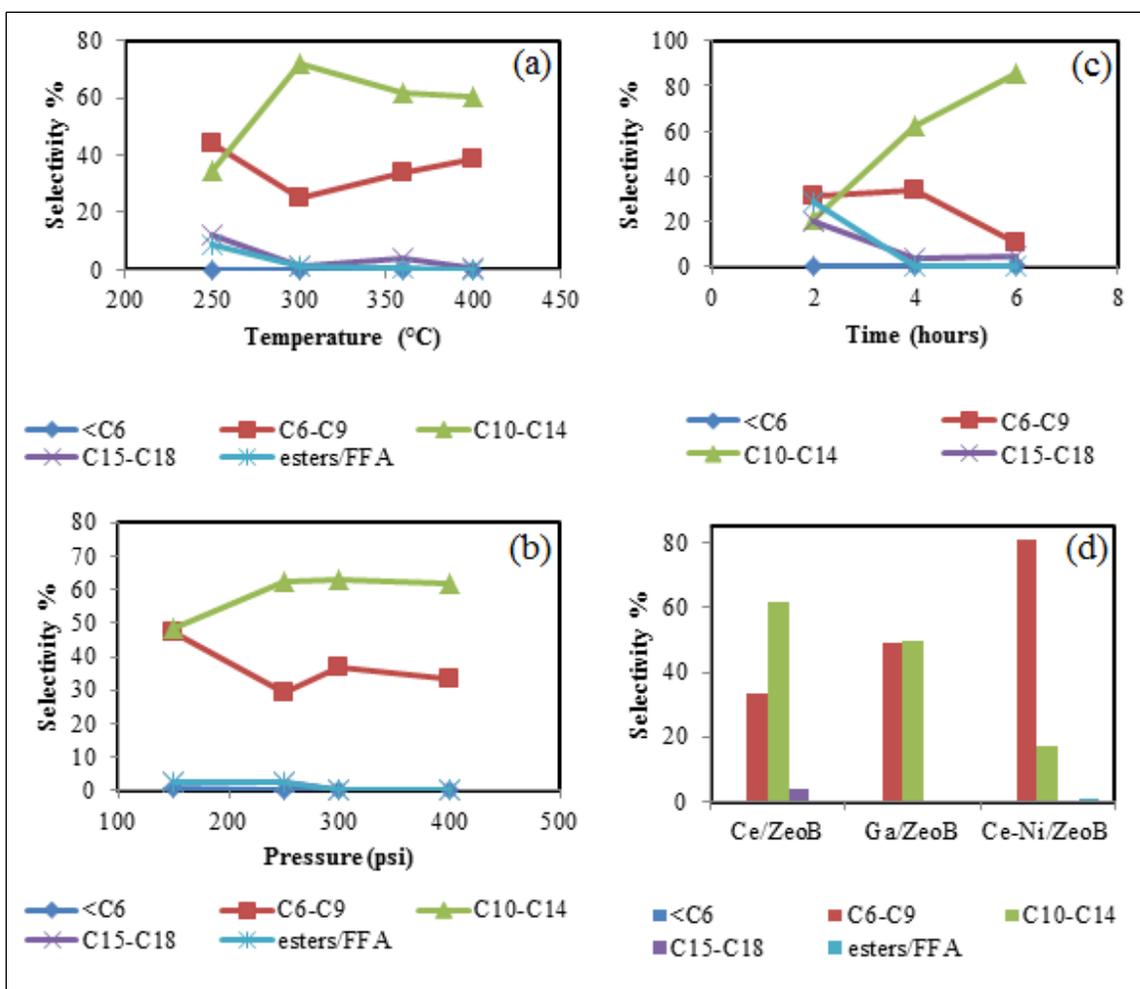
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$$n - C_N \qquad CH_3 - C_{N-1} \qquad diCH_3 - C_{N-2} \qquad triCH_3 - C_{N-3} \qquad tetraCH_3 - C_{N-4}$$

$$\updownarrow \qquad\qquad \updownarrow \qquad\qquad \updownarrow \qquad\qquad \updownarrow \qquad\qquad \updownarrow$$

$$n - C^-{}_N \;\leftrightarrow\; CH_3 - C^-{}_{N-1} \;\leftrightarrow\; diCH_3 - C^-{}_{N-2} \;\leftrightarrow\; triCH_3 - C^-{}_{N-3} \;\leftrightarrow\; tetraCH_3 - C^-{}_{N-4} \;\leftrightarrow$$

$$\downarrow\updownarrow$$

$$CH_3 - C_{N-1-M} + n - C_M$$

$$\downarrow\updownarrow$$

$$CH_3 - C_{N-1-M} + n - C_{M-1} \qquad\qquad \downarrow\updownarrow$$

$$etc..$$
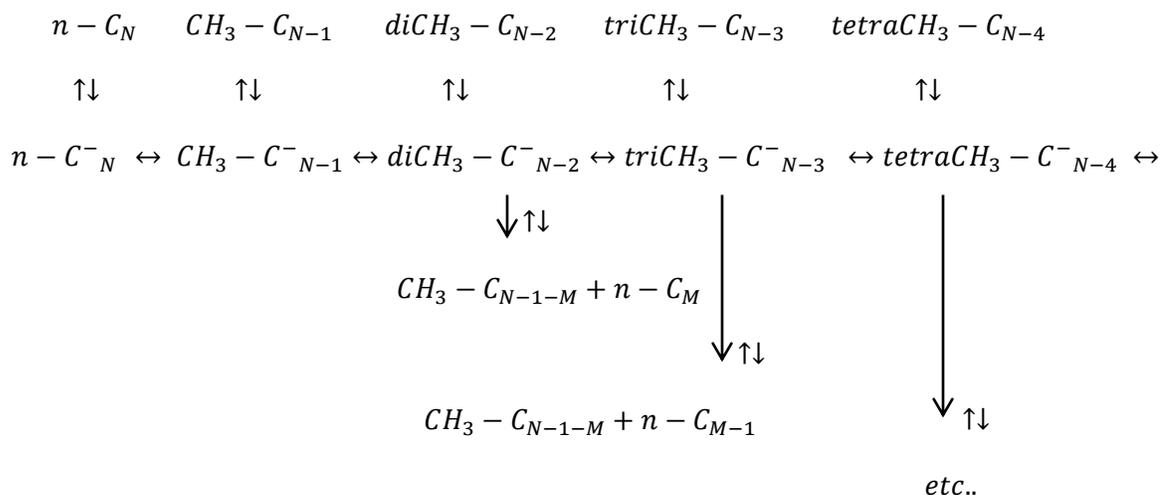
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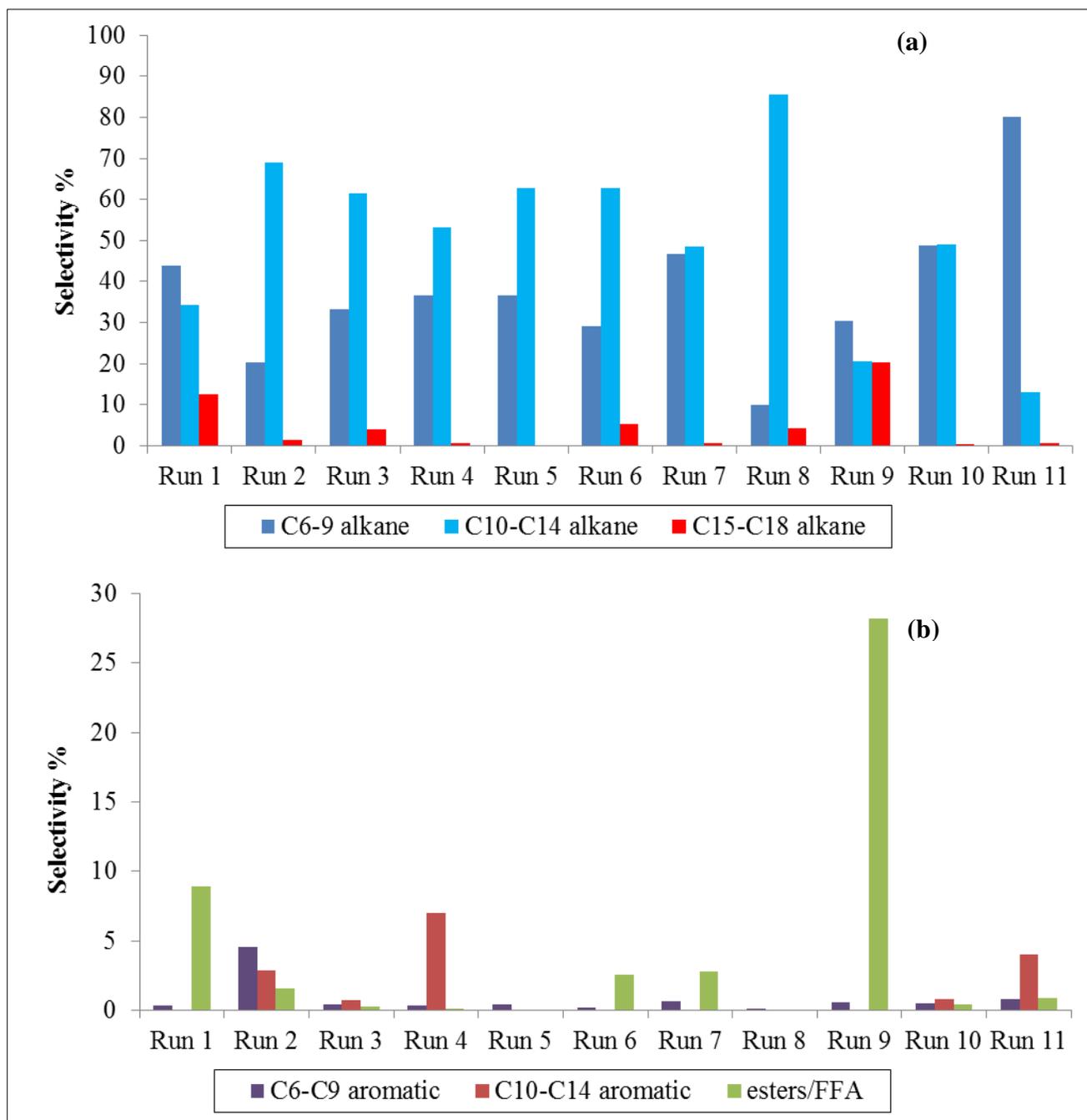
Figure 8. The selectivity for the reaction for the formation of various alkanes and aromatics for reactions conducted using Ce exchanged zeolite β as catalyst (a) selectivity towards alkanes and (b) selectivity towards aromatics.

Feedstock oil	Reaction conditions	Catalyst	Hydrocarbon range	Reference
Safflower	T=340°C	Pt/ NiMoC on SBA-15	C5-C14	71
	P=142 psi		Conversion: 25%	
	t=3 hours			
Jatropha	T=350°C	NiAl/LDH	C8-C17	72
	P=101 psi		Conversion: 74%	
	t=4 hours			
Used cooking	T=390°C	Ni/ γ-Al$_2$O$_3$	C10-C15	63
	P=1200 psi		Conversion: 20%	
	t=20 hours			
Rapeseed	T=400°C	NiMo/Al$_2$O$_3$	C7-C18	73
	P=1595 psi		Selectivity: 80%	
	t=3 hours			

Table 1. Reactions conditions for hydrotreating various types of triglycerides along with free fatty acids and their product compositions.

Run no.	Temperature (°C)	Pressure (psi)	Time (h)	Catalyst
1	250	400	4	Ce/ZeoB
2	300	400	4	Ce/ZeoB
3	360	400	4	Ce/ZeoB
4	400	400	4	Ce/ZeoB
5	360	300	4	Ce/ZeoB
6	360	250	4	Ce/ZeoB
7	360	150	4	Ce/ZeoB
8	400	400	6	Ce/ZeoB
9	360	400	2	Ce/ZeoB
10	360	400	4	Ga/ZeoB
11	360	400	4	Ce-Ni/ZeoB

Table 2. Variables used in the experimental set: time, temperature, pressure and catalyst. Catalyst and feedstock quantity were maintained constant at 0.1 g and 10 g, resepctively

Hydrocarbons identified using GC-MS	
Cyclopentane	Cyclohexane
Hexane	Dodecane
Octane	Tetradecane
Nonane	Octyl-cyclohexane
Decane	Nonyl cyclohexane
Undecane	Decyl-cyclohexane
Tridecane	Hexadecane
Pentadecane	Heptadecane
O-xylene	Nonadecane
Eicosyl-cyclohexane	Heptyl-cyclohexane
Eicosane	

Table 3. Hydrocarbons identified in the liquid fuel samples subjected to GC/MS analysis following hydrocracking.

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