



INVESTIGATION OF METALLIC OXIDE CATALYST ROLE FOR UP GRADING BIODIESEL TO BIO JET FUEL RANGE HYDROCARBON

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ABSTRACT

This article investigates the upgrading of biodiesel produced from palm oil using different metallic oxide catalysts under relatively mild conditions. Upgrading experiments were conducted at 300°C, under pressure (3 bar) for 3 hours using 2.5 % catalyst dose (wt. /vol.), at 60 rpm stirring rate in a high-pressure reactor. The employed catalysts are Ni/HZSM5, calcium zinc aluminate, and zinc aluminate. It was found that zinc aluminate ($ZnAl_2O_4$) is an efficient and stable catalyst for cracking long chain hydrocarbons in biodiesel to alkanes. High yield of short chain hydrocarbons were obtained, (50.09% jet fuel, 41.34% diesel fuel range hydrocarbon and zero gasoline range hydrocarbon). The upgraded biodiesel was subjected to elemental analysis and GC mass analyses. In addition, physical properties of upgraded biodiesel like viscosity, density, high heating value (HHV) were determined. It was found that more aromatization and isomerization occurs and increases C_8-C_{15} range, which is a jet fuel range hydrocarbons to about 51% using $ZnAl_2O_4$. However, preceding the reaction in the presence of hydrogen for more de-oxygenation resulted about 43% $C_8 - C_{15}$. The activity and selectivity of ($ZnAl_2O_4$) for jet fuel range hydrocarbon showed high yield after product distillation process at about 280°C.

Keywords: Jet-fuel, bio - oil, catalytic upgrading, cracking.

1. INTRODUCTION

Energy shortage and increase in fuel consumption make it must to find alternative sources of bio-fuels to cater these needs [1]. Nowadays the main fuel sources are hydrocarbons, which are depleting. About 79% of energy need all over the world is provided from fossil fuels according to Energy Information Administration (US Energy Information Administration 2009).

Recently bio-fuels have gained international attention as alternative to traditional fuels because they are friendly environment due to their high degradability, no toxicity, and low harmful emissions [2, 3]. Therefore, it is necessary to search for renewable energy sources to produce sustainable and efficient bio-fuels. Bio - jet fuel can be produced by isomeration of hydrocarbons over different heterogeneous catalyst [4]. One of the most important conversion process to get both fuels and chemical products and converting large bio-oil molecules to short chain hydrocarbons from bio-sources is the thermal catalytic reaction [5-10]. Thermal cracking of hydrocarbons is performed at 800- 850 °C [11], while lower cracking temperature produces lower flame temperature that causes elimination of NO_2 emissions [11]. Main constituents of jet-fuel are aromatics and cyclic - hydrocarbons because they are of high energy - density [12]. Therefore, it is difficult to produce these constituents using conventional technologies for bio- fuel production without upgrading for further aromatization and isomerization [12]. Hydro cracking and isomerization of linear alkanes reduce their molecular weight and increase fuel stability by introducing branching [13,14].

Upgrading of biodiesel can be conducted using different types of catalyst, but heterogeneous catalysts were preferred to avoid the neutralization and separation

steps [15-20]. Some of these catalysts like Zinc aluminate, can be regenerated and reused in three reaction cycles with the same activity [21]. Zinc aluminates are widely used as a catalyst or support in cracking, acetylation, transesterification and dehydrogenation processes [17, 19, 22-25]. This article is investigating upgrading and refining of biodiesel to produce jet fuel using three different types of heterogeneous catalyst that can be easily separated and reused. Catalyst namely Nickel supported acidic Zeolite (Ni- HZSM-5) [12], Zinc Aluminate ($ZnAl_2O_4$) [26], and Calcium addition on Zinc Aluminate (Al-Ca- Zn) [27] were prepared in this work.

2. EXPERIMENTAL

2.1. Materials

All metal nitrates (Zn, Al, Ca, and Ni) and acidic zeolite (HZSM5) are analytical grade. Methanol (99.9%), Potassium hydroxide (98.9%) and Ammonia solution (28wt %) are purchased from EL-Nasr company, Egypt.

2.2. Transesterification of palm oil to biodiesel

The biodiesel was prepared using KOH as homogeneous catalyst (0.7%w/v) and methanol (2.5%v/v) with palm oil at 65°C for 2 hours. Then the produced methyl ester was separated from glycerol, washed with 5% warm acetic acid. Table-1 illustrates the physic-chemical properties of palm oil.

**Table-1.** Physico chemical properties of palm oil.

Parameter	Value
Viscosity at 40°C	41 MPas
Density	0.88 kg/L
Acidity	0.3 mg KOH/g oil
Pour point	3°C
Cloud point	9°C
C	71.33wt%
H	21.75wt%
O	5.64wt%
N	0.28wt%
S	Nil
<C ₅ (%)	5.54
C ₅ -C ₇ (%)	2.4
C ₈ -C ₁₅ (%)	18.52
C ₁₆ -C ₁₉ (%)	16.71
>C ₁₉ (%)	56.84

2.3. Catalysts preparation

Zinc aluminate

Co-Precipitation method was performed using mixed solutions of zinc nitrate, Zn(NO₃).6H₂O (24gm in 40 ml. distilled water) and aluminum nitrate, Al(NO₃)₃.9H₂O(60gm in 40 ml distilled water) [26]. Ammonia solution was added to the previous solution with

stirring till complete precipitation. The precipitated gel was filtered, washed with distilled water and dried at 110° C for 24 hours. The dried solid was calcined at 750 °C for 3.5 hours to obtain zinc aluminate (ZnAl₂O₄) catalyst.

Ni/Zeolite (Ni/HZSM5) catalyst

Nickel was stabilized by impregnating it on acid zeolite (HZSM5) at 650°C for 4 hours [12].

Calcium zinc aluminate

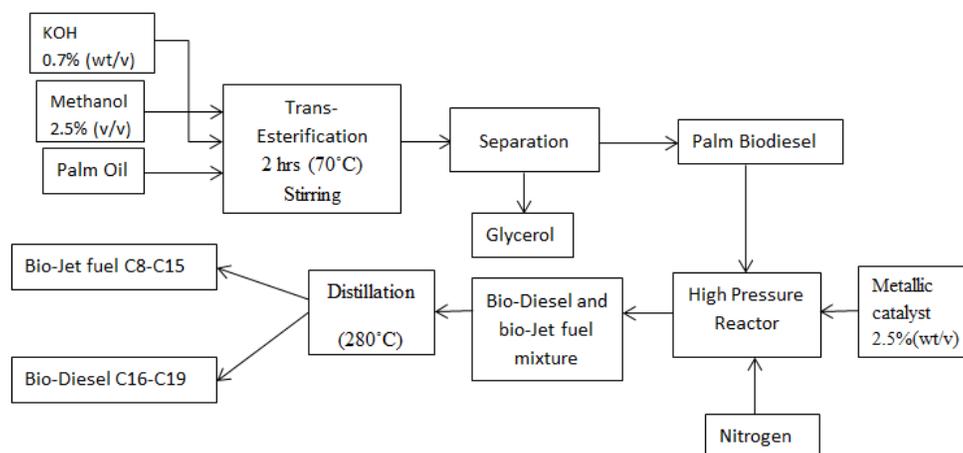
Co-precipitation method was performed from metal nitrate of Ca, Zn & Al at Ph=8 [27]. The gel obtained was dried and calcined 800°C for 8 hours.

2.4. Experimental set-up

Experimental work was carried on floor-stand reactor under pressure (Parr reactor).The reactor includes stainless steel (316) vessel (3.7 L capacity), pressure gauge and a heating jacket provided with mechanical stirrer. The temperature inside the reactor was controlled by proportional integral derivative panel (PID).

2.5. Upgrading process using different solid catalysts

Reaction vessel was charged with 360 ml biodiesel from palm oil and 9 gm catalyst (2.5% w/v), stirred at 65r.p.m for 20 min after passing nitrogen for ten minutes at ambient temperature, then adjusting temperature to (300°C). The pressure was elevated with the rise in temperature for holding time of reaction (3h). At the end of reaction time, cooling the reactor then collect the reaction mixture. Same previous steps were repeated for the used other two catalysts, and these experimental steps are illustrated in Figure-1.

**Figure-1.** Block flow sheet for upgrading process using different solid catalysts

2.6 Hydrogenation and distillation of upgraded bio-oil

Same last experimental steps were repeated but with introduction of hydrogen to the reactor after air removal by passing nitrogen then preceded the rest of the experiment. Upgraded bio-oil was distilled using a distillation unit to separate jet fuel (C₈-C₁₅) as a distillate

and diesel (C₁₆-C₁₉) as a bottom product using 265 ml of upgraded oil at certain temperature.



3. RESULTS AND DISCUSSIONS

3.1 Preparation of biodiesel

The palm oil is transesterified using 20% (v/v) of methanol and 0.7% (wt. /v) of KOH. The palm biodiesel is produced from transesterification process in addition to glycerol as a by- product. Table-2 illustrates Physico chemical properties of palm biodiesel.

3.2 Pressure and temperature profiles inside the reactor

Figures 2 and 3 show the pressure and temperature profiles during upgrading of the biodiesel inside the high-pressure reactor. Heating-up takes around 100 min then the pressure remains constant around 3.3 bars for about 180 min thereafter. The average temperature was 300°C and the average pressure are 3.3 bars. The pressure and temperature throughout all experiments were oscillating around the same value, which indicates that the upgrading results are just an indication of the catalyst effect.

Table-2. Physico chemical properties of palm biodiesel.

Parameter	Value
Viscosity at 26.5°C (M Pas)	9.97
Density at 15°C (Kg/L)	0.925
Cloud point (°C)	13
Pour point (°C)	9
C (%)	68.92
H (%)	21.88
O (%)	8.6
N (%)	0.601
S (%)	Nil
<C ₅ (%)	0
C ₅ -C ₇ (%)	0.07
C ₈ -C ₁₅ (%)	6.79
C ₁₆ -C ₁₉ (%)	92.78
> C ₁₉ (%)	1.06
HHV (MJ/Kg) ⁽²⁸⁾	43.57

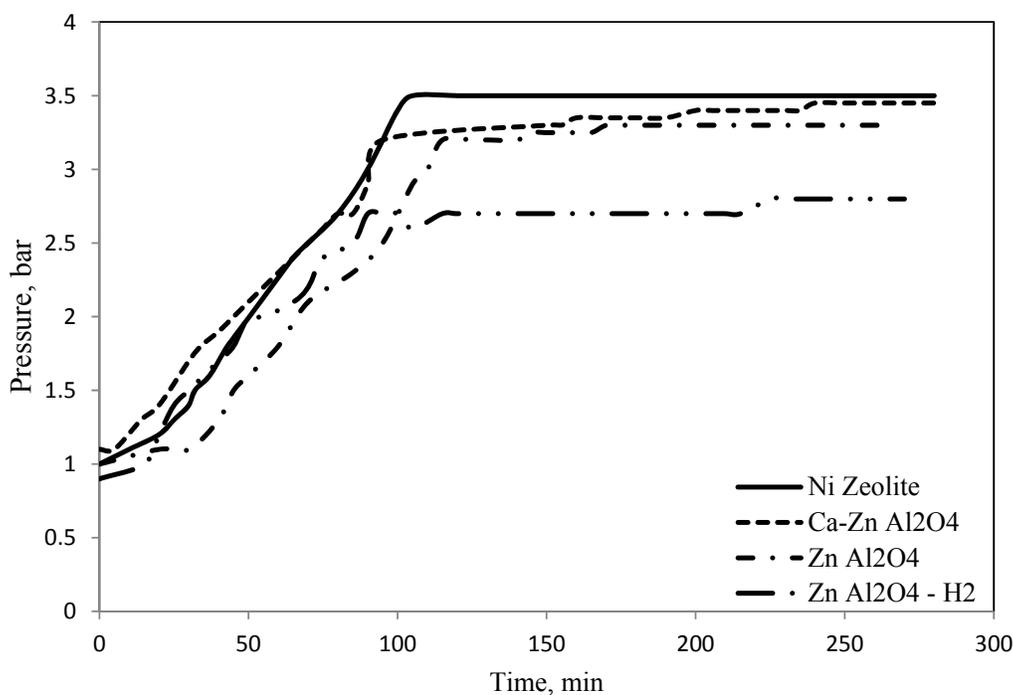


Figure-2. Pressure inside reactor during the upgrading experiment.

3.2. Upgrading of palm biodiesel

The composition of palm biodiesel is mostly diesel range hydrocarbon C₁₆-C₁₉ as shown in Table-2. To

upgrade the produced biodiesel, the biodiesel is subjected to cracking reaction using different catalysts at 300°C under a pressure of 3.3 bars; the detailed flow sheet is



shown in Figure-1. The products from cracking are shown in Table-3, noting that the best results from cracking is represented using $(ZnAl_2O_4)$ catalyst.

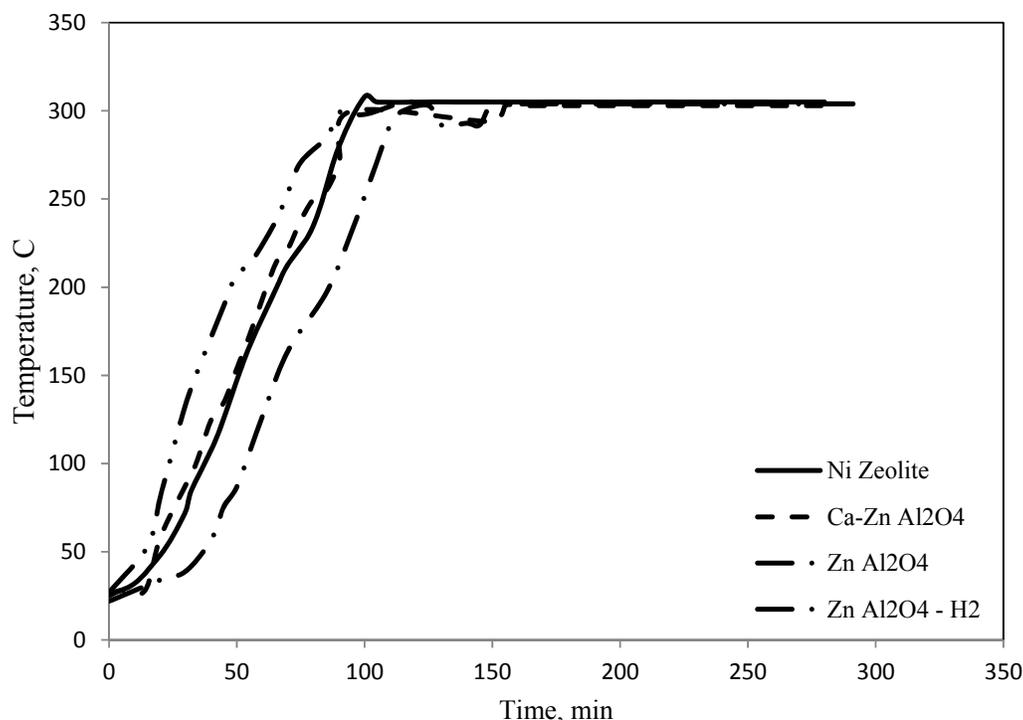


Figure-3. Temperature profile inside the Parr reactor during the upgrading experiment.

Table-3. Composition of range hydrocarbon from GC-Mass of upgraded biodiesel using different catalysts.

catalyst composition	Ni/Zeolite	CaZnAl ₂ O ₄	ZnAl ₂ O ₄ without hydrogen	ZnAl ₂ O ₄ with hydrogen
<C ₅ %	0	0	0	0.05
C ₅ -C ₇ %	0	0	0	0.05
C ₈ -C ₁₅ %	15.97	50.09	47.08	43.26
C ₁₆ -C ₁₉ %	79.17	41.34	44.88	23.78
> C ₁₉ %	5.2	8.56	8.59	32.87

Noting that C₅ - C₇ are the main composition for gasoline range alkanes while C₈ - C₁₅ are main constituents of jet fuel range alkanes and C₁₆-C₁₉ are components of diesel range alkanes [4]. Table (4) represents the results of distillation products from cracking experiments using ZnAl₂O₄ as a catalyst with and without hydrogen. From the results in Table-3, it is clear that: percent of C₁₆ - C₁₉ (biodiesel range alkanes) decreases from 92.78% of palm biodiesel by up-grading without hydrogenation to 79.17%, 41.34% and 44.88% using Ni/Zeolite, CaZnAl₂O₄ and ZnAl₂O₄ catalyst respectively then to 23.78% by using ZnAl₂O₄ with hydrogenation.

From Table-4 it is clear that the percent of biodiesel range alkanes C₁₆-C₁₉% was reduced to 23.78%

and 10.53% after distillation of up-graded product using ZnAl₂O₄ catalyst with and without hydrogenation respectively. All the results indicated that biodiesel after treatment with different catalyst is converted partially to jet fuel and distillation has efficient performance to improve quality of refined biodiesel (deep hydro de-oxygenation), which means that distillation of biodiesel has produced a distillate containing 92.55%, C₈-C₁₁, and C₁₆ - C₁₉ decreased to 10.53% using CaZnAl₂O₄ as catalyst at 280°C. While using hydrogen in the reaction (HDO), C₁₆ - C₁₉ content decreased to 23.78% as shown in Figure-4.



Table-4. Composition of range hydro carbon from GC-Mass of distilled upgraded biodiesel using catalysts ($ZnAl_2O_4$) with & without hydrogen.

composition	Distillate $ZnAl_2O_4$ without hydrogen	Distillate $ZnAl_2O_4$ with hydrogen
<C5 %	0	0.096
C5-C7%	0	2.19
C8-C15%	88.94	46.63
C16-C19%	10.53	14.25
> C19%	2.12	38.68

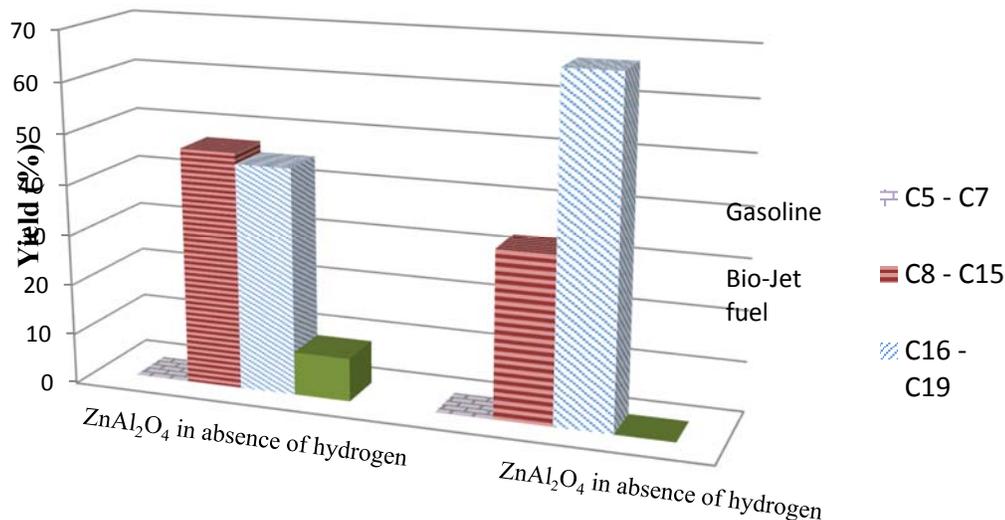


Figure-4. Diesel Jet fuel and Gasoline range hydrocarbon via $ZnAl_2O_4$ catalyst with/without hydrogen.

Results of elemental analyses are illustrated in Table-5, from which it is clear that by comparing oxygen content, distillation of upgraded biodiesel without hydrogen decreased sharply from 8.31% to 0.24.

Modified Dulong equation is used to calculate the higher heating value [28]

$$HHV = 4.18 * (78.4 * C + 241.3 * (H - O / 8) + 22.1 * S)$$

Table-5. Elemental analyses and Higher Heating Values (HHV) of biodiesel and upgraded bio-oils using different catalysts.

Compos ition (wt. %)	Palm oil	Biodiesel of palm oil	Upgrading (Ni/Zeolite)	Upgradin g ($ZnAl_2O_4$)	Upgradi ng $CaZnAl_2O_4$	Distillate of upgrading ($ZnAl_2O_4$) without hydrogen	Upgrading ($ZnAl_2O_4$) with hydrogen	Distillate upgrading ($ZnAl_2O_4$) with hydrogen
C	67.13	68.92	62.61	62.41	60.41	70.71	60.61	69.33
H	24.95	21.88	28.32	29.02	30.02	28.8	29.25	20.75
O	7.64	8.6	8.74	8.31	9.1	0.25	9.58	9.44
N	0.28	0.6	0.33	0.26	0.47	0.24	0.56	0.48
S	NIL	NIL	NIL	NIL	NIL	NIL	NIL	NIL
C/H	2.6905862	3.149992	2.210885	2.150585	2.012325	2.455	2.07213	3.34120
HHV ⁽²⁸⁾ (MJ/Kg)	42.9738	43.570	47.98	48.675	48.93	52.19	48.16	42.46



Three catalysts used for upgrading were Ni/HZSM-5, $\text{CaZnAl}_2\text{O}_4$, and ZnAl_2O_4 . A better performance is observed with $\text{CaZnAl}_2\text{O}_4$ and ZnAl_2O_4 , similar performance has been observed for both catalysts. Comparing C/H weight ratios we notice that using ZnAl_2O_4 as catalyst gave C/H ratio less than that of crude palm biodiesel or that for biodiesel upgraded using Ni/HZSM5. Which indicate that the product of upgrade biodiesel via ZnAl_2O_4 was not only aromatic compound but more saturated alkanes since aromatic product resulting from the decrease of acid sites on the surface of the catalyst [12]?

3.3. Distillation of upgraded biodiesel

The distillation column is used to separate jet fuel ($\text{C}_8\text{-C}_{15}$) as a distillate and diesel ($\text{C}_{16}\text{-C}_{19}$) as a bottom product at 280-300°C. Starting with 265 ml of upgraded biodiesel, a distillate of around 56% is produced containing 87% of jet fuel ($\text{C}_8\text{-C}_{15}$). From GC-Mass it was found that the major constituents of jet fuel hydro carbon range ($\text{C}_8\text{-C}_{15}$) were paraffinic compounds 95.5% while cyclic and aromatic constituents were 3.5% and 1% respectively which is a good agreement with previous studies[29].

A bottom product of 44% is produced containing diesel ($\text{C}_{16}\text{-C}_{19}$). The results have indicated that bio-jet fuel can be produced using ZnAl_2O_4 as a catalyst under mild reaction conditions and using a distillation column to separate the required range hydrocarbon. This work represents a successful application of bio-refinery to produce jet fuel range.

4. CONCLUSIONS

- Very promising results were obtained using zinc aluminate (ZnAl_2O_4) as catalyst in upgrading palm biodiesel to Jet-fuel.
- The reduction in viscosity indicates that water content is also reduced which leads to increase in HHV.
- Ni/HZSM-5 produced less bio-aviation range hydrocarbons when it is used to upgrade palm biodiesel.
- Loading calcium mass on zinc aluminate do not improve obviously the bio-jet hydrocarbon range.
- The produced hydrocarbon via zinc aluminate as catalyst was mainly branched alkanes and cyclo-alkanes with a maximum yield $\approx 89\%$ after upgrading and distillation processes.
- Distillation of upgraded biodiesel without hydrogenation had efficient performance to improve quality of refined biodiesel.

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