

## CATALYTIC CRACKING OF SOYBEAN OIL WITH ZIRCONIUM COMPLEX CHEMICALLY BONDED TO ALUMINA SUPPORT WITHOUT HYDROGEN

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[Received-14/06/2012, Accepted-23/06/2012]

### ABSTRACT:

A homonuclear macrocyclic Zr–Zr complex was prepared starting with 2,6-diformyl-phenol and 1,2-phenylene diamine and is chemically bonded with carbamate-modified alumina. The present study deals with the use of this complex catalyst in the catalytic cracking of vegetable oil such as soybean oil without hydrogen. The catalytic cracking reactions of vegetable oils such as soybean oil was carried out using the complex catalysts Zr–Zr covalently bonded with alumina in absence of H<sub>2</sub>. Literature search from deoxygenation reaction suggest that this reaction in presence of H<sub>2</sub> is straight forward and the products are formed in high yields. However, in absence of H<sub>2</sub> various catalysts reported produced over seventy components giving gases (such as CO, CO<sub>2</sub>), non condensable organic gases (such as methane to butane), unsaturated vinyl gases and liquids, aromatics and oil residues. With the use of our complex catalyst, we found only liquid product with total absence of residues and noncondensable gases. The GC-MS analysis of the liquid product showed the formation of only five fatty acids (stearic acid, palmitic acid, oleic acid, linoleic acid and linolenic acid), aldehyde (decanal) and alkane [(3 ethyl-5-2 (-ethyl butyl) octadecane and one alkene 1-octadecene. The number of components, this way, reduced considerably with the absence of residues and noncondensable gases. The product distribution depended upon the temperature and as the temperature increased, the yield of alkane product also increased.

**Keywords:** Catalytic cracking, Soybean oil, Vegetable oil, Alumina, Complex catalyst, Zirconium.

### [I] INTRODUCTION

Due to rapid growth of economic development, there is an increase in consumption of energy and simultaneous reduction in the availability of earth's natural resources (such as fossil fuels) and out of the total energy consumed as fossil fuels

(80.3%), the transport sector consumes 57.7% of it. Nowadays, because fossil fuels are burnt for energy and exhausted, the exhaust gas being mostly CO and CO<sub>2</sub>, due to these gases green house effect produces which is a matter of great concern for environmentalists. On using fuels

derived from biomass, emission of CO and CO<sub>2</sub> tend to balance out leading to reduction in green house effect. Biodiesel is derived from vegetable oils and is attracting increasing attention worldwide as blending component or as direct replacements for fuel in vehicle engines. There are several methods for the conversion of vegetable oils to biofuels, such as pyrolysis, gasification, transesterification processes, catalytic cracking reaction, and hydrocracking reaction etc. Among these methods, the catalytic cracking of vegetable oils to produce biofuels has been widely studied by many researchers over the world. However, the use of this method on industrial scale is limited by the high cost, formation of several unwanted byproducts etc. and availability of vegetable oil feedstock (75% of the total manufacturing cost) [1-3].

One of the major advantages of using biodiesel is that it is a biodegradable material and is environmentally beneficial. The major obstacle to widespread use of biodiesel is the high cost relative to fossil feedstock and it exhibits poor cold flow properties, which can be problematic for engine performance, and increased NO<sub>x</sub> emission. The presence of oxygen lowers the heat content indicated by the heating values of biodiesel, which are 9%-13% lower than those of conventional diesel fuels on a mass basis.

If the oxygen is eliminated by pyrolysis or catalytic cracking, one can obtain gasoline, diesel, oil and light olefins which can partially replace the commercial petroleum products in future. The cracking can be performed in fluidized bed reactor, laboratory-scale once-through microriser reactor or transport riser reactor. Higher yield of liquid can be obtained in the products with fixed-bed reactor, but the olefinic content of gas product is much lower. In view of this, Two-stage riser fluid catalytic cracking (TSRFCC) technology has been adopted which has considerable flexibility of meeting various production goals and has been tested in pilot plant by several scientists [4]. Several

studies exist in literature on thermal as well as catalytic deoxygenation of vegetable oils and reaction pathway for palm oil has been reported in reference [5]. With the use of ZSM-5 catalyst, the conversion of the oil leads to a product mixture having more than atleast seventy components consisting of heavy hydrocarbon and oxygenates and the GCMS studies has identified light alkanes, alkenes, water, carbon dioxide and carbon monoxide. Light alkenes can also undergo oligomerization to produce a mixture of heavier alkenes and alkanes which are categorically arranged under gasoline, diesel and kerosene fractions. The aromatic hydrocarbons were produced by aromatization, alkylation and isomerization of heavier olefins and paraffins. Coke is also produced in sufficient amount by direct condensation of palm oil and polymerization of aromatics [6].

There are several other studies on catalytic cracking of vegetable oil and results indicate technical viability to produce fuels similar to petroleum based fuels under right processing conditions. The conversion of vegetable oil produces several gaseous products, does not form a well defined product and cost of production at the moment is high [7-12].

As an alternative to the catalytic cracking discussed above the deoxy-liquefaction is used to obtain hydrocarbon oil under constant temperature of 400 °C and fixed residence time of 20 min. The hydrocarbon oil obtained was similar to that of diesel oil and the GCMS analysis of this product has shown the presence of several gases (e.g. CO and CO<sub>2</sub>) and at least sixty more liquid components. Effect of catalyst, temperature and residence time has been examined and the results of these studies indicate that the oil products were sharply affected by temperature and for low temperatures, diesel like product was obtained in greater yield. In presence of catalyst H-ZSM 5, alkane content of foil increased to as much as 55.38 % and unlike the

effect of temperature, the effect of residence time on the product was relatively very small [13].

### [II] MATERIALS AND METHODS

#### 2.1. EXPERIMENTAL SECTION

The catalytic cracking reaction of vegetable oils has been carried out in batch reactor made of stainless steel of 500 ml volume. The reactor is equipped with pressure gauge to monitor pressure in the reactor, a thermocouple to measure the temperature inside the reactor, gas delivery system and provision for sampling. An on/off temperature controller has used for controlling the temperature with a chrome alloy thermocouple for temperature sensing. 100 ml of vegetable oil is fed into the reactor along with 2 gm of catalyst. The reactor is then closed and allowed to heat upto the desired temperature limit for reaction. In our case the reaction is carried out in the temperature range of 250-450 °C using catalyst.

#### 2.2. CATALYST SYNTHESIS

Homo dinuclear zirconium macrocyclic complex was synthesized. For this, we first prepared 2,6-diformyl-4-methyl phenol following the procedure given in literature [14]. For the preparation of the complex, two equivalents of 2,6-diformyl-4-methyl phenol was condensed with two equivalents of 1,3-diamino propane to obtain the ligand.

##### Synthesis of macrocyclic [Zr-Zr] complex:

ZrL<sub>2</sub>' : To 50 ml of N, N-dimethylformamide at 40 °C, 2,6-diformyl-4-methylphenol (1.95g, 0.012 moles) is added first, followed by drop wise addition of (0.5 ml, 0.006 moles) of 1, 3 diaminopropane with stirring. To this solution (2.5g, 0.006moles) of zirconium oxichloride is added and the solution is stirred till all the zirconium oxichloride dissolves completely (step I of figure 1). The solution is kept for 1 h after which diethyl ether (50ml) is added following which a precipitate appears which is filtered and dried.

Zr-ZrL<sub>2</sub>' : The ZrL<sub>2</sub>' (1.9g, 0.0045moles) obtained from the previous step is dissolved in 30 ml of methanol and to this, (0.9g, 0.0045moles) of zirconium oxichloride dissolved in methanol is added with stirring (step II of figure 1). After 1h, diethyl ether (50ml) is added and within 30 minutes olive green precipitate is formed which was filtered and dried.

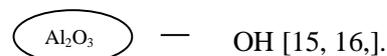
ZrZrL<sub>2</sub>: The ZrZrL<sub>2</sub>' (1.83g, 0.0038 moles) was dissolved in 30 ml of methanol and to this, a solution of 1,3 diaminopropane (0.3ml) is added drop wise with stirring. The solution is kept for 30 minutes and then diethyl ether (50ml) is added to it (step III of figure 1). A precipitate is formed which is filtered from the solution and dried.

##### Preparation of supported catalyst:

Following four steps are involved in modifying the alumina support for catalyst loading.

##### 1. Drying the Alumina Beads

The alumina after drying at 500°C for 8h is found to have a number of hydroxyl groups on its surface and these are schematically shown as



2. Preparation of carbamate alumina: Phenyl isocyanate is prepared by the reaction of sodium azide (35g, 0.4mol) with benzoyl chloride (70 ml) for 8 hours in presence of dry benzene (20ml) at 0°C [17]. Sodium azide is taken in a flat-bottomed flask with dry benzene and kept in an ice bath. Benzoyl chloride is added drop wise with stirring. The reaction is carried out for eight hours. The reaction mixture is vacuum filtered and permeate obtained is collected. Dried alumina is reacted with phenyl isocyanate for four hours at ambient conditions. The isocyanate reacts with the OH present on alumina giving O-C-NH groups on its surface.

3. Modification of carbamated alumina by reacting with 1, 2-dichloroethane: Carbamated alumina (3g) is reacted with 50ml dichloroethane in presence of ZnCl<sub>2</sub> (5 mg) at 80°C for two hours. The product is then washed with dichloroethane and dried. The ethylene chloride

reacts at the phenyl end of the carbamate alumina, thereby giving a chlorine group on alumina which can then be made to react with the complex molecule.

4. Preparation of catalyst by covalently bonding complex to modified alumina: The complex is dissolved in methanol and reacted with modified alumina at 60°C for 4-6 hours. The loaded catalyst is washed and dried which gives the desired catalyst.

### [III] RESULTS AND DISCUSSIONS

Soybean oil was subjected to catalytic deoxygenation without hydrogen in a batch reactor and by procedure discussed in experimental section and products obtained were palmitic acid (OA<sub>1</sub>), stearic acid (OA<sub>2</sub>), oleic acid (OA<sub>3</sub>), linolenic acid (OA<sub>4</sub>), linoleic acid (OA<sub>5</sub>), an aldehyde (decanal) and 3 ethyl-5-2 (-ethyl butyl octadecane (abbreviated as OD<sub>1</sub>), which is a C<sub>18</sub> alkane and 1-octadecene (abbreviated as OD<sub>2</sub>), which is a C<sub>18</sub> alkene.. These products formation was confirmed by GC-MS.

The individual concentration of different fatty acid has been plotted in **FIGURE 2**. For soybean oil using Zirconium complex catalyst at 350 °C, we see that dominant concentration is for OA<sub>2</sub> and OA<sub>5</sub>. The concentration of these are small upto 140 min but then quickly rises beyond this time while the concentration of OA<sub>1</sub>, OA<sub>3</sub> and OA<sub>4</sub> remain less than 10% for all times. In **FIGURE 3**, the yield of all fatty acid has been combined and at different temperature after 4 h of reaction has been recorded. It was found from figure 5.6 that the reaction did not occur below 250 °C while at 400 °C reaction, considerable amount of gases is generated. However the reactor pressure on cooling goes down to atmosphere pressure which suggests that one can assume that only water or methanol was formed which condense on cooling. However, for temperatures beyond 450 °C, a residual pressure always existed at ambient conditions indicating

that there is formation of CO<sub>2</sub> and CO gases during the decomposition of oil. This implies that for temperature less than 400 °C, only decarbonylation reaction occurred while for temperatures at above 400 °C, decarbonylation as well as decarboxylation reactions have occurred. In **FIGURE 4**, it is assumed that the fatty acid are present in reaction mass are all isomers then they can be treated as single component.

Experiments show that the total yield of fatty acid (**FIGURE 3** and **4**) is negligible before 250 minutes after this time of reaction, amount of fatty acid present in the reaction mass rises quickly and takes on a high value of about 80-90%. The total yield of fatty acid after 250 minutes of reaction as a function of temperature has been plotted in figure 5.7 and it is seen that the yield increases linearly with temperature. The third component of the catalytic reaction of oil has been identified to be decanal (C<sub>9</sub>H<sub>19</sub>CHO). The yield of decanal versus time is plotted in **FIGURE 5** and it is found that temperature less than 300 °C, the formation of this is negligible and at 300 °C, the product just begins to form. At 350 °C and reaction time of about 160 minutes, the concentration of decanal begins to increase rapidly but does not go beyond 6% at any time of reaction. Looking at this figure, it is suggested that fatty acid is formed first, but for larger times it becomes an aldehyde as a series reaction due to loss of moisture from fatty acid.

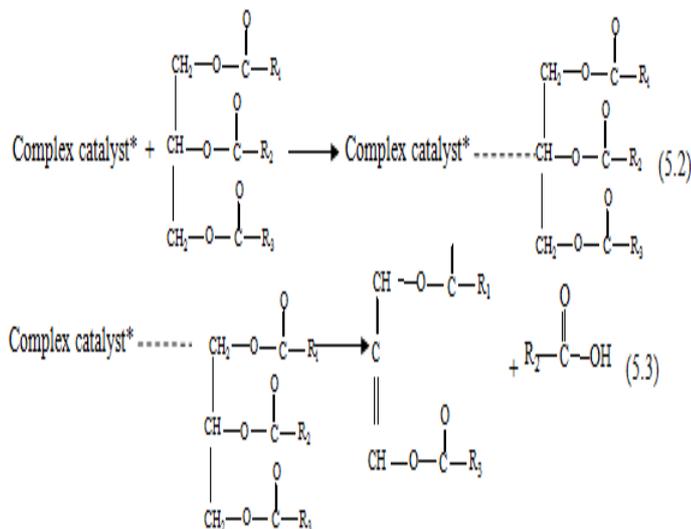
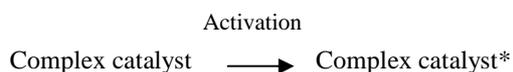
The concentration of both peaks (OD<sub>1</sub> and OD<sub>2</sub>) has been combined in **FIGURE 6** and the combined result for C<sub>18</sub> alkane and alkene has been plotted. It is seen that for temperature less than 400°C, the total amount of C<sub>18</sub> alkane and alkene formed is small and always remain less than 5%. However, for temperature 450°C the formed OD increases suddenly giving an increase in the reactor pressure. When reactor is cooled to room temperature, the reactor pressure also does not go back to zero as observed for temperature less than 400°C. This implies that alkane is also getting formed by decarboxylation reaction and it

leads to a release of CO and CO<sub>2</sub> as result of which reactor pressure does not go back to zero on cooling.

In **FIGURE 6**, we have plotted the total yield of C<sub>18</sub> alkane and alkene as function of time with temperature as a parameters and we notice that as temperature increases, the yield continues to reduce (in contrast to yield of fatty acid which increase with temperature. It may be observed that at 250 °C, there is no reaction at all and at 300 °C the amount of C<sub>18</sub> components in reaction mass is close to approximately 70% which continued to fall with increase in temperature.

The extensive data on the catalytic cracking of oil has been reported in this chapter and product identification has been carried out using the GC-MS. This analysis has revealed the fact that the reactor pressure rises during reaction and on cooling goes back to ambient pressure and there is complete absence of CO and CO<sub>2</sub> and other noncondensable gases. The product analysis reveals considerably fewer products consisting of fatty acids (palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid), aldehyde (decanal), alkanes (3 ethyl-5-2 ethyl butyl octadecane and alkene (1-octadecene). The results show the cleaving of C-C bond and the most surprising result is the presence of the fatty acids in that -CO bond in acid functional group were preserved during the reaction.

In order to explain our experimental results, it is necessary that the oil must be complexing with the catalyst of the C-O bond on glyceryl moiety forming activated state as follows:



The acid functional group of fatty acid is preserved because due to complexation the energy needed to break the covalent bond has become less than that needed for breaking the -CO bond.

Repeated reaction of this would lead to depolymerization of the chain alongwith giving fatty acid formation. Next important thing, to observe is that in all the results reported in this chapter the product concentrations increase initially reaching an asymptotic value for large times of reaction. This implies that the overall reaction is either reversible in nature or is limited by the availability of the starting material. On looking the data and the nature of reaction, most likely, cracking reaction occurs fast enough and the asymptote arises purely because of non availability of reactants. The next question which must be answered is whether the product formed further undergone any reaction. It is observed in all consecutive reaction of the A→B→C, then concentration of B is suppose to reach maximum with C appearing with a time delay. In our case no product behaves like the concentration of B in this consecutive reaction. For high temperatures, the aldehyde formation occurs and the appearance of the aldehyde has time delay and is most likely to form from the fatty acid that we have produced initially as a sequential reaction.

Since there is no CO and CO<sub>2</sub> formed in the cracking reaction, it clearly indicates that the acid group of this fatty acid does not break during the course of reaction and the dehydrogenation of fatty acid is the only reaction which forms aldehyde. The alkane formation should definitely be occurring due to the breakage of C-C bond and not the breakage of -COOH group of the fatty acid.

#### [IV] CONCLUSIONS

The literature search on deoxygenation of oils has been carried out which reports that in presence of H<sub>2</sub>, the deoxygenation can be easily carried out using suitable metal salts catalysts. It is desired to carry out this reaction without H<sub>2</sub> and the literature reports, the product distribution to be extremely large. This consists of noncondensable gases such as CO, CO<sub>2</sub>, H<sub>2</sub>O vapors, methane to butane, several aldehydes and aromatic compounds. The total species were to above 70 components as confirmed by the GC-MS analysis. We have been used heterogeneous complex catalysts cracking of oil without using H<sub>2</sub>. The product did not contain any noncondensable gases and the GC-MS analysis of liquid, thus formed, was shown to have five fatty acids (stearic acid, palmitic acid, oleic acid, linoleic acid and linolenic acid), aldehyde (decanal) and four number of alkanes (3 ethyl-5-2 (-ethyl butyl) octadecane and one alkene (1-octadecene). On increasing reaction temperature, we find that the total content of alkanes increases at the cost of reduction of total fatty acids formed.

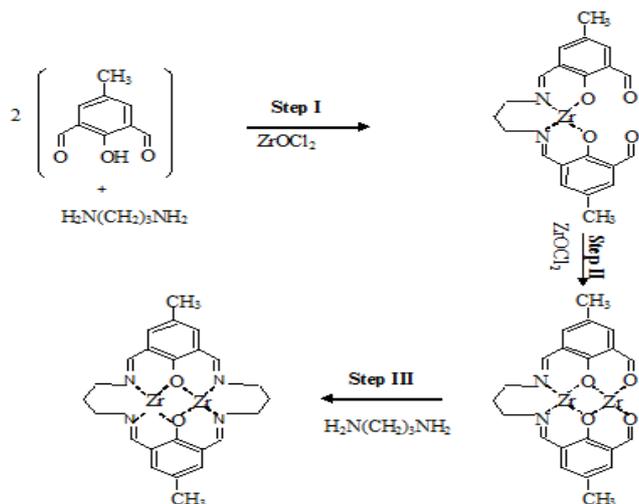
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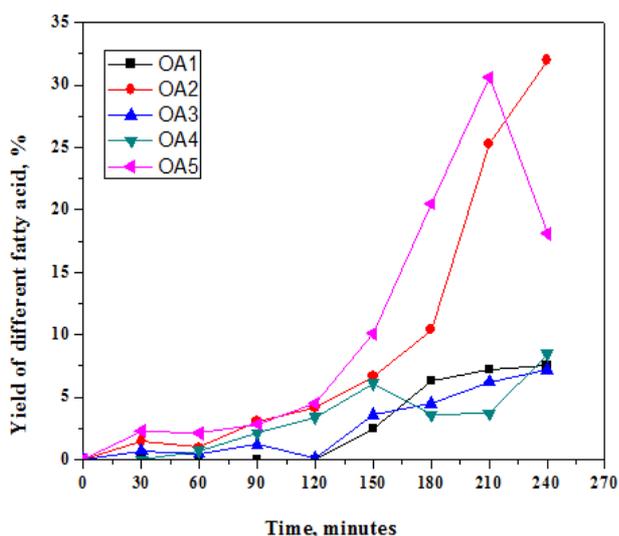
CATALYTIC CRACKING OF SOYBEAN OIL WITH ZIRCONIUM COMPLEX CHEMICALLY BONDED

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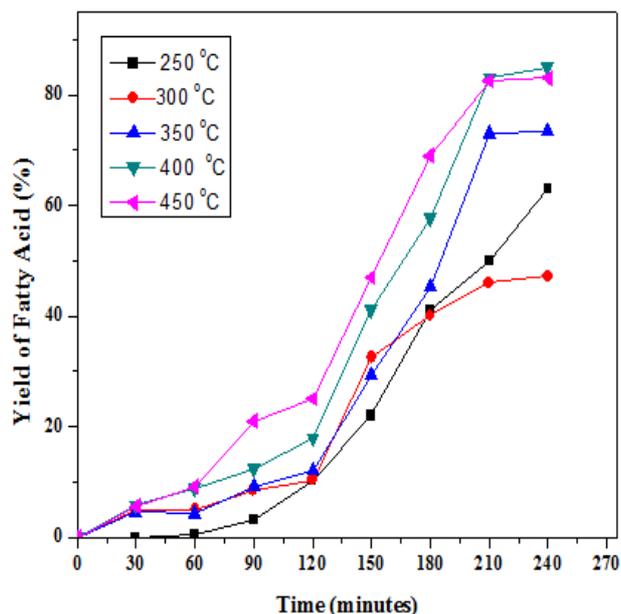
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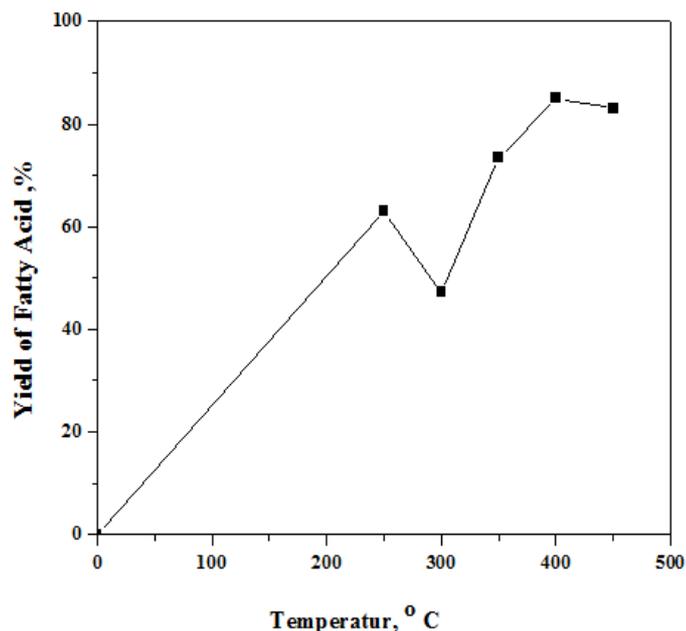
**Figure 1.** Synthesis of homodinuclear macrocyclic Zirconium complex



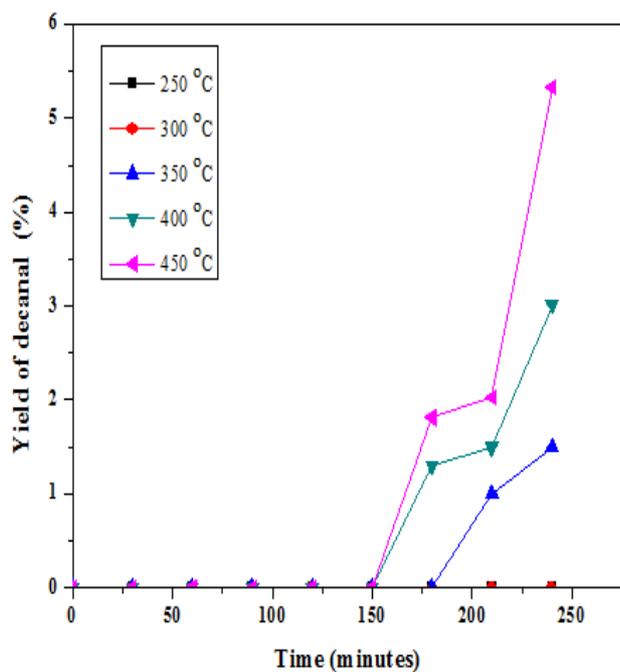
**Figure 2.** Yield of different fatty acids vs time with Soybean Oil using  $[\text{Zr-Zr}]\text{L}_2/\text{Al}_2\text{O}_3\text{-HPA}_{\text{M}_0}$  at  $350^\circ\text{C}$



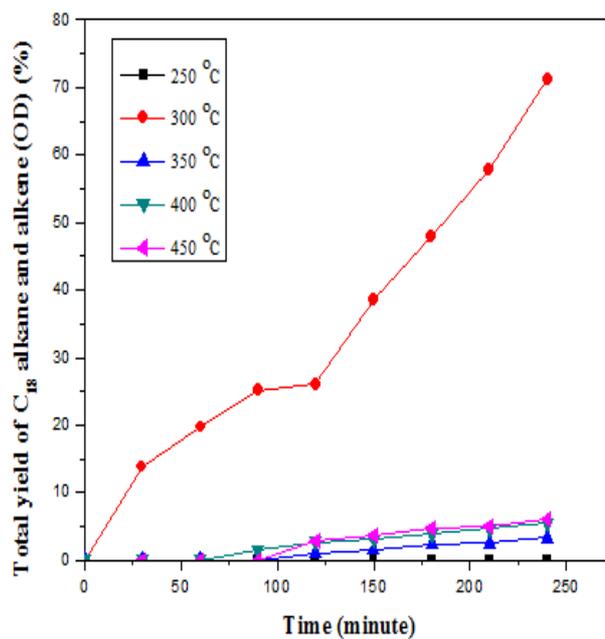
**Figure 3.** Yield of Fatty acid vs time with Soybean Oil using  $[\text{Zr-Zr}]\text{L}_2/\text{Al}_2\text{O}_3\text{-HPA}_{\text{M}_0}$  at different temperature with reaction time 4 h.



**Figure 4.** Yield of Fatty acid vs temperature with Soybean Oil using  $[\text{Zr-Zr}]\text{L}_2/\text{Al}_2\text{O}_3\text{-HPA}_{\text{M}_0}$  with reaction time 4h



**Figure 5.** Yield of decanal vs time with Soybean Oil using  $[Zr-Zr]L_2/Al_2O_3-HPA_{M_0}$  at different temperature



**Figure 6.** Total Yield of  $C_{18}$  alkane and alkene vs time Soybean Oil using  $[Zr-Zr]/Al_2O_3-HPA_{M_0}$  at different temperature.