Clean fuel production by deoxygenation of pure palmitic acid using Ni/Al$_2$O$_3$ catalyst.

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Abstract: Removal of oxygen from fatty acid in the form CO$_2$ and CO to produce diesel like hydrocarbon (green diesel) was proceeded via catalytic deoxygenation process through decarboxylation and decarbonylation reaction. This reaction was studied over non noble metal catalysts 20wt%Ni/Al$_2$O$_3$ and performed in batch reactor system (autoclave) by using pure palmitic acid, n-hexane as a solvent and 200psi pressure. The effect of different atmospheres (pure hydrogen, pure nitrogen, and mixture of 50 psiH$_2$/150psiN$_2$) and different temperature range (300^{0}C-350^{0}C) under a mixed atmosphere (50 psiH$_2$/150psiN$_2$) were studied in this paper. The main product was n-pentadecane (C$_{15}$) which the catalyst Ni/Al$_2$O$_3$ has lower cracking selectivity to light hydrocarbons. The results indicated that as the temperature increases the total conversion and the selectivity for (C$_{15}$) increase to (99.61%) and (85.54%) respectively which the presence of hydrogen in atmosphere gas improved catalytic performance. so the catalyst displayed high activity and operation selectivity. Analysis of liquid products by gas chromatography (GC) was used to determine n-alkane (C$_{15}$) yield and other products (isomeres, olefins and dimers). The catalyst 20wt%Ni/Al$_2$O$_3$ with surface area (236.376 m^2/g) was prepared using deposition precipitation method and the characteristics of the catalyst were investigated.

Keywords: Fatty acids, Catalytic deoxygenation, Ni catalysts, Green diesel.

1- Introduction.

Now a days due to depletion of fossil fuel reservoirs, increasing crude oil prices and the environmental pollution including global warming these reasons increasing the need for energy production and encouraging the search for fuel alternative to fossil fuel.[1] Large attention for production of biofuel from renewable sources have been taken in the recent years. The most important way to get fuel fungible with fossil fuels is to use fatty acids and their derivative to produce fuel.[2] There are many alternative techniques recently developed to produce biofuels such as transesterfication, the thermal and catalytic cracking (pyrolysis). The Catalytic cracking method is used to break down high molecular weight compounds to fragments of lower molecular weight but this process is highly unselective and yields a number of undesirable compounds mainly oxygenates. [3] The transesterfication method is used to convert renewable feed stock to the fatty acid methyl esters (FAMEs) known as biodiesel. While biodiesel has good lubricity and cetane number biodiesel behavior is less ideal than transportation fuel[4] which has high viscosity, pour point, undesirable poor storage stability, cold flow properties and low heating value because it has high oxygen content and unsaturation of chain compared to fossil

fuel, also corrosion problems occurred due to the presence of Free fatty acids remaining in products and produces amount of glycerol as a byproduct,.[5] Anovel method for production of fuel compatible with diesel derived from fossil fuel is the deoxygenation process.[6] That process produce fuel like hydrocarbon that composed of n-alkanes and alkenes that are hydrocarbons similar to those found in diesel fuel and the product has high quality and free from sulfur and oxygen.[7] Deoxygenation of fatty acids and their derivatives (DO) is a general term covers all reactions involving the removal of oxygen from a molecule, this will generally be in the form of water, carbon dioxide or carbon monoxide.[8] and including hydrodeoxygenation or decarboxylation / decarbonylation of carboxylic group which leads to formation of diesel like hydrocarbons (green diesel).[9] Hydrodeoxygenation of free fatty acids is the main process for production of fuel composed of hydrocarbons containing the same carbon number as the feedstock by using hydrogen to eliminate oxygen in the form of water but the high cost of hydrogen increase the cost of the production method and it used sulfide catalyst that make contamination of product and need to handle it carefull.[10,11] Recently, alternative method, in which hydrogen is not a necessity or used in a little amount is the

decarboxylation/decarbonylation of fatty acids producing a straight-chain hydrocarbons having one carbon less than the original fatty acids (n-1), CO_2 or CO and water by using simple catalyst. [12,13] The presence of small amount of H_2 increase the catalytic activity of catalyst by decreasing the undesirable compounds that form coke and lead to deactivation of catalyst.[14] Early work by Murzin and coworkers in the period (2005–2008) studied the deoxygenation of saturated and unsaturated fatty acids and their derivatives under inert atmosphere (Ar, N2, and He) and in the presence of hydrogen. They screened supported metal catalysts Ni, Ru, Ir, Pt, and Rh for deoxygenation of stearic acid (dissolved in dodecane) in semi-batch reactor and found that the carbon-supported palladium was the most promising catalyst.[15] Later research found that Pd/C catalyst deactivates rapidly in the deoxygenation of SA in the absence of H_2. [16] Crocker and coworkers studied the deoxygenation of triglyceride (tristearin) and fatty acid (stearic acid) through decarboxylation/decarbonylation (deCOx) in a semi-batch reactor over 5 wt.%Pd/C and 20 wt.% Ni/C and found that both catalysts afforded good yields of diesel-like hydrocarbons but 5 wt.% Pd/C showed higher selectivity to C17.[17] Deoxygenation of fatty acids is a difficult task because of the rapid catalyst deactivation, low reaction rate and saturated fatty acids (with more than nine carbon atoms) have a high melting point so the reactor must be heated. In this paper we study deoxygenation reaction of palmitic acid over 20wt%Ni/Al_2O_3 in batch autoclave and using different atmosphere pressure, different temperature and n hexane solvent. Which the cost of Ni is 1000 and 2500 times lower than that of Pd and Pt, respectively.

2- Experimental.
2-1 Materials.
The materials used were: Al $(NO_3)_3.9H_2O$ (> 97% purity), $Na_2(CO3)$ (> 97% purity), Ni $(NO_3)_2.6H_2O$(> 97% purity), HNO_3 acid 69 %, urea, palmitic acid, n-hexane and deionized water.
2-2 Catalyst preparation.
2-2-1 Preparation of gamma alumina (support).
The support was performed in a 5 liter beaker. 500 ml deionized water was heated to 70°C in the beaker. Then Al $(NO_3)_3.9H_2O$ (200 g) was dissolved in 1000 ml (1 L) deionized water and Na_2 (CO_3) (101.85 g) was dissolved in1000 ml (1 L) deionized water also. The aluminum nitrate solution and the sodium carbonate solution were added to 500 ml deionized water by burette. The mixture was stirred vigorously to form an aluminum hydroxide gel. The temperature was kept at 70°C during the reaction. After precipitation happened, adding sodium

carbonate was continue till the mixture attained a pH range of 8- 8.5. The produced colloidal solution was aged at 70°C while stirring constantly for overnight. The obtained gel was separated from the mixture by 4000 rpm centrifugation for 15 min. The pH of filtrate was 11. Then white gel was washed several times (20 min. each time) with de-ionized water at70°C till pH of the filtrate attained a pH of about 5.5 and then dried in oven at 120°C overnight. The dried sample was milled. After that the dried product was treated in tube furnace by a programmed calcination. The heating rate was maintained at 2°C/min from room temperature to 550°C that inferred from TGA analysis in static air and maintained at 550°C for 1 hour then it was cooled to the ambient temperature.

2-2-2 Preparation of catalyst (20wt% Ni/Al_2O_3).
The alumina support was functionalized with nickel using a deposition-precipitation method. In this procedure, 250 ml of an aqueous solution containing 13.065g of Ni $(NO_3)_2.6H_2O$ and 0.3 ml of HNO_3 69 % wt/wt was prepared. In a typical preparation, 40 ml of the aqueous solution was used for dissolving 10.012 g of urea at room temperature to make a urea solution and 210 ml of the aqueous solution was mixed with 11.022 g of the gamma alumina support to make a suspension. The suspension was heated at 40 °C, and then mixed with the urea solution under rapid mixing. After that, the mixture was heated to 90°C for 8 h under static condition then aging and reflux for 24 h. After cooling, the mixture was filtered and the solid was washed several times with hot deionized water (~50°C) followed by drying at 120°C for 12 h. Then, the solids were calcined in tube furnace. The heating rate was maintained at 2°C/min from room temperature to 550°C in static air and hold on 550°C for 4 h. Then the calcined samples were reduced in tube furnace at 360°C for 4 h under hydrogen stream by ramp *(5°C /min)*, and then cooled to room temperature then put in a desicator.

2-3 Catalyst characterization.
Thermal analysis (TGA).
Thermo-gravimetric analysis of the dried sample was conducted in TGA/DTA and carried out by using a thermal gravimetric analysis instrument (pyres, Diamond Thermo gravimetric). The compounds were heated in a nitrogen atmosphere from 0-1000°C controlling the heating rate of about 10°C/ min. This showed the various decomposition occurring in the dried precursor as a function of temperature and we could decide the calcination temperature of the as-dried precursor.

X-ray diffraction (XRD).
The X-ray Diffraction (XRD) studies were performed on the dried sample, the support (gamma alumina) and the catalyst (Ni/Al_2O_3) in order to identify the phases present and their crystallinity. X-

ray diffraction (XRD) measurements were performed with graphite monochromatic CuKα (λ=1.54056 Å) in the scanning angle (2θ) range 0-100°.

Fourier Transforms Infrared (FTIR) Spectroscopy.

FTIR spectroscopy were performed on the dried sample, the support (gamma alumina) and the catalyst (Ni/Al_2O_3) in order to obtain detailed information about the molecular structure of the catalysts. FTIR spectroscopy for the test materials was carried out by KBr disc technique using a Fourier transform infrared spectrometer; Varian (Model: FTS-800) FTIR in the range 4000–400 cm^{-1}

Nitrogen adsorption and desorption isotherm data obtained at -196 ^0C.

The BET surface areas and pore volumes were performed on the support (gamma alumina) and the catalyst (Ni/Al_2O_3)) and measured by nitrogen adsorption and desorption isotherm data obtained at -196 °C on a constant-volume adsorption apparatus using Quantachrome Nova 3200 S automates gas sorption apparatus. Prior to the measurement, the samples were degassed at 200°C overnight to remove the moisture and impurities adsorbed on the catalyst surface and pores before analysis, and then the samples are switched to the analysis station for adsorption and desorption under a temperature of -196 °C in liquid nitrogen. The adsorption isotherms were recorded in the pressure range (P/P0) <0.3 sufficient to characterization of the micro and mesopore region. The specific surface areas (S_{BET}, m^2g^{-1}) of the samples were calculated according to the Brunauer, Emmett and Teller (BET) method.

Determination of acidity.

The Determination of acidity of the catalyst (Ni/Al_2O_3) was performed by using pH electrode in an aqueous catalyst slurry. The slurry of catalyst was stirred with a magnetic stirrer, while pH was registered and monitored. After reaching a constant pH value the acidity was determined.

2-4 Deoxygenation experiments:

The deoxygenation experiments were carried on model fatty acid such as palmitic acid by using batch reactor. Palmitic acid: It is a saturated fatty acid with formula: $C_{16}H_{32}O_2$, Mol.wt: 256.42 and Melting point: 61-62.5 °C.

Deoxygenation experiments were performed in a mechanically stirred 500 mL stainless steel autoclave operated in batch mode.

2-4-1 Firstly reduction of catalyst.

The catalyst (1 g) in powder form was reduced in situ under flowing H_2 stream for and for 4h (at 360°C for Ni/Al_2O_3) then the reactor was purged with N_2.

2-4-2 Deoxygenation process.

After reduction of catalyst the autoclave was cooled. Both solvent (200 ml n-hexane) and feedstock (10 g palmitic acid) were added to the autoclave then autoclave was purged several (3-5) times with N_2. After that the reactor was pressurized with the required gas atmosphere and heated to the required temperature. The reactor was kept at the selected temperature for 6h. The reactor temperature was measured by a type-K Omega thermocouple placed inside the reactor body. The reactions were performed under mechanically stirred at 1000 rpm. The gas stream exiting the reactor was cooled with a condenser kept at room temperature in order to recover any volatile products in the gas stream. When the reactor reached room temperature, reaction product and catalyst were removed from the reactor and separated by gravity filtration to isolate the products. The recovered solids were then extracted twice with hexane to yield additional material. After separation of catalyst from the reaction products, the reaction products were put in oven to evaporate the solvent (n-hexane).

2-5 Product analysis.

The liquid phase products were analyzed with:

Gas chromatography (GC Agilent 7890A) equipped with flame ionization detector (FID), mobile phase (carrier gas) was N_2 and HP-5 column (length 30 m, internal diameter 0.32 mm, film thickness 0.25 Mm). The following temperature program was used for analysis: 50°C (10 min) by ramp4°C /min to 300 °C (20min).

3- Results and discussion
3-1 Catalyst characterization.
3-1-1 Thermal analysis (TGA).

The thermal behavior of the dried boehmite was studied by DTA/TGA analysis and the experimental curves are shown in (Fig 1). Two major endothermic weight losses were observed in DTA curve at 63.3^0C and at 260^0C. The first may be due to removal of physically adsorbed water, while the second weight loss at 260^0C is attributed to dehydroxylation and nitrate decomposition, other broad exothermic peak at 475^0C with a very minor weight loss in DTA curve may be ascribed to crystallization transition of alumina. The total weight loss of 33.20 % occurs during the three step decomposition process, showing that the decomposition of aluminium hydroxide to alumina has occurred. [18]
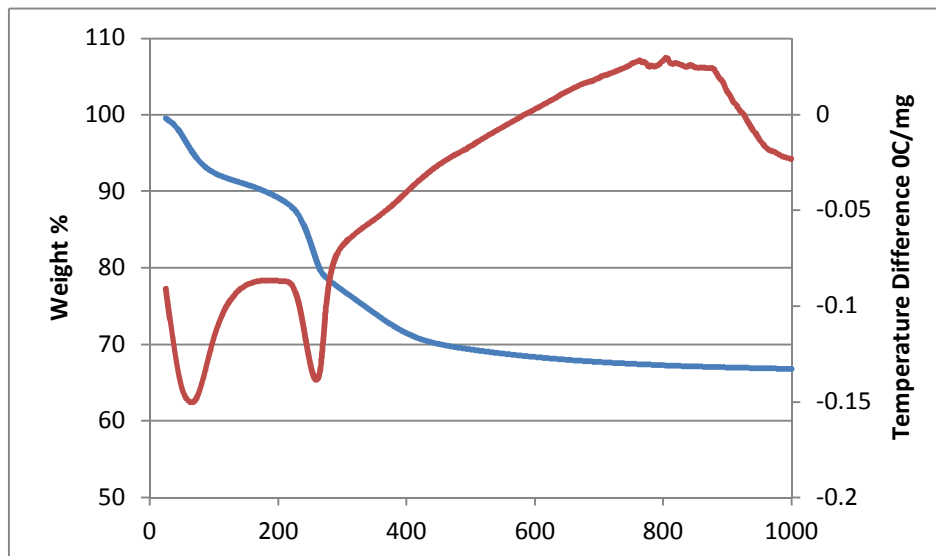
Fig (1) DTA/TGA curves the dried boehmite.

3-1-2 X-ray diffraction (XRD).

The phase identity and crystallinty of the catalyst were revealed throughout the XRD patterns. Fig (2 a, b) depicts XRD patterns for the gamma alumina and gamma alumina supported Ni prepared by deposition precipitation.

Fig. 2-a shows the XRD patterns of powder obtained by calcination of as dried boehmite at $550C^0$. Fig. (2-a) revealed three peaks at 37.5^0, 46^0 and 67^0 assigned to the gamma alumina phase. However, all reflections shown in Fig.(2-a) are indexed for the reported gamma alumina having spinel lattice [00-029-0063]. The crystallite size calculated using scherrer equation. The broadening of XRD peaks revealed the nano size nature of gamma alumina particles in these samples.[19]

Fig(2-b) revealed that the XRD diffraction pattern of supported Ni/Al_2O_3 catalyst which exhibited diffraction peaks at 37.3^0, 44.3^0 and 62.7^0 correspond to Ni and $NiAl_2O_4$ [00-001-1260], this suggesting that catalysts are associated with both dispersed and bulk nickel oxide or nickel.[20]
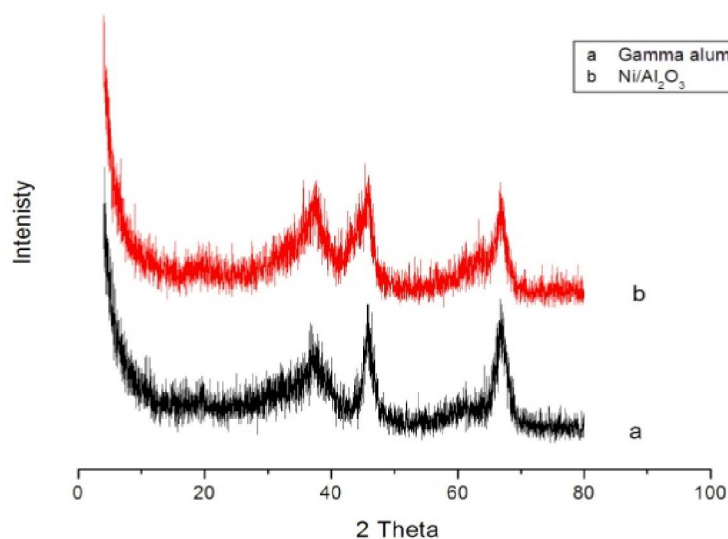
Fig (2) XRD of a- the gamma alumina, b- Ni/Al_2O_3

3-1-3 FTIR-spectroscopy.

FTIR studies on as dried boehmite (Fig 3-a) and its calcined powders (Fig 3-b). Figure 3-a shows FTIR spectrum which reveals a strong and wide band centered around 3470 cm^{-1} and a broad band at 1634 cm^{-1}, these are referred to stretching and bending modes of absorbed water. The band in the range of 1490-1410 cm^{-1} and 880-860 cm^{-1} were missed, suggesting that the dried boehmite does not contain any carbonate ion (CO_3^{-2}). The Al-O-Al bending stretching vibrations observed at 1070 cm^{-1} is due to symmetric bending mode. The OH torsional mode observed at 735 cm^{-1} overlaps with Al-O stretching vibration. The week band at 2091 cm^{-1} is assigned to combination band.[21] The bands observed at 626 and 518 cm^{-1} are attributed to stretching and bending mods of AlO_6.[22] The band at 1387 cm^{-1} seen in (Fig3-a) is corresponding to NO_3^{-1} ion or OH stretching due to presence of adsorbed water, this peak was completely removed after calcination. In the spectrum of calcined powder showing in (Fig 3-b), the peaks in the region of 500-750 cm^{-1} are assigned to v -AlO_6, and the shoulder at the region of 890-800 cm^{-1} are referred to v-AlO_4. Thus gamma alumina phase contains both tetrahedral and octahedral coordination. The broad peak at 3470 cm^{-1} and the weak band at 1634 cm^{-1} are due to adsorbed water. [23]
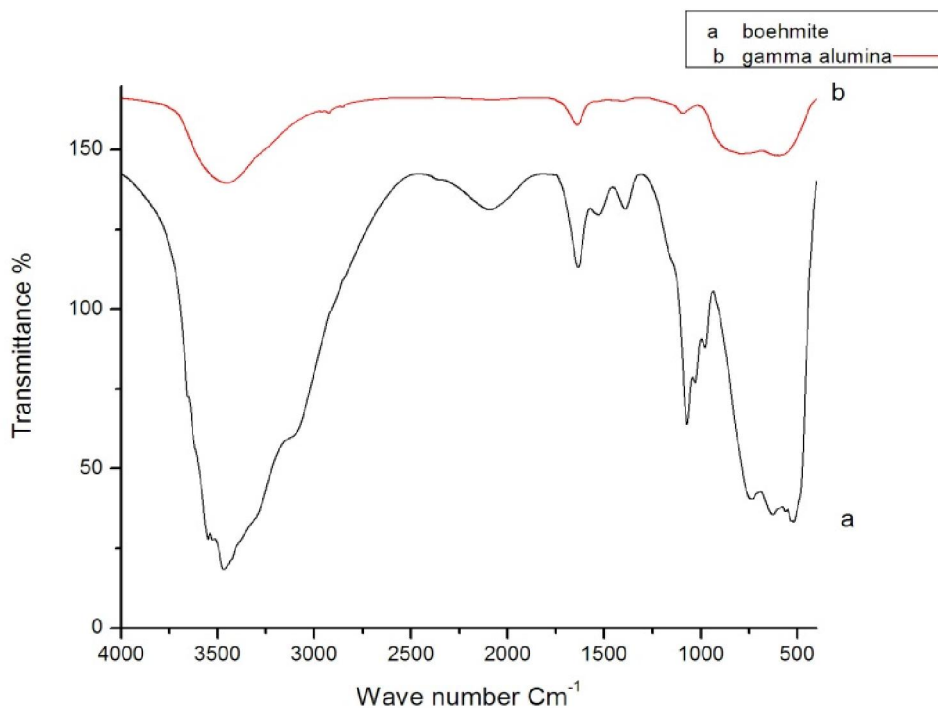

Fig (3) FTIR of a- the dried boehmite, b- gamma alumina

3-1-4 Surface area.

The surface area, pore size distribution and pore volume of pure gamma alumina and nickel supported gamma alumina (20wt%Ni/Al_2O_3) are shown in Table (1).

Catalyst	Surface area (m^2/g)	Average pore size (nm)	Total pore volume (ml/g)
Alumina (support)	243.92	8.57	0.53
20wt%Ni/Al_2O_3	236.38	7.86	0.46

The surface area 243.917 m^2/g was observed for pure gamma alumina, while that of the nickel supported catalyst revealed 236.376 m^2/g as observed from the Table (1), the surface area of supported catalyst was slightly less than that of pure support due to increasing nickel loading on gamma alumina, This may be due to coverage of surface area of gamma alumina and blockage of pores by nickel or nickel
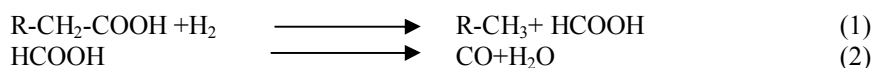
oxide. [24] So that, the total pore volume decreased from 0.53 to 0.46 ml/g. The pH of catalyst is (4.2). The activity of catalyst depends on pH value of the aqueous catalyst slurry which slightly alkaline properties are preferred but tends to form aromatics whereas acidic catalysts did not form aromatics and causes some cracking.[25]

3-2 Deoxygenation of palmitic acid over 20wt% Ni/Al$_2$O$_3$.

3-2-1 Deoxygenation of palmetic acid under three different atmospheres.

The deoxygenation of palmitic acid were performed over 20 wt% Ni/Al$_2$O$_3$ under three different atmospheres namely pure hydrogen, 50/150 hydrogen/nitrogen mixture and pure nitrogen at 300^{0}c for 6 hours have been studies. The results were represented in table (2) The results in table (2) indicate that the total conversion of carboxylic groups of palmitic acid and the selectivity to C$_{15}$ in case of pure hydrogen are(28.35% and 64.3%) respectively and in case of pure nitrogen they are (21.49% and 32.5%) respectively while in case of H$_2$/N$_2$ mixture the total conversion and the selectivity are (69.1% and 60.22%) respectively for Ni/Al$_2$O$_3$catalyst as given in Figs.(7and8). It is clear that the total conversion of carboxylic group and selectivity of C$_{15}$ is higher in the presence of pure hydrogen than that in case of pure nitrogen. This is due to that hydrogen promotes hydrogenation and curbs the catalyst inhibition caused by the adsorptions of deposits formation. With an increase in hydrogen pressure the contribution of the decarbonylation reaction increases[26] as the following equations.

$$R\text{-}CH_2\text{-}COOH + H_2 \longrightarrow R\text{-}CH_3 + HCOOH \qquad (1)$$
$$HCOOH \longrightarrow CO + H_2O \qquad (2)$$

Carbon monoxide produced may adsorbed on the catalyst surface before it can be removed from the system and inhibiting the deoxygenation of palmitic acid by the catalyst. Also, CO is known to dissociate on Ni sites and give rise to carbon deposits, the accumulation of which can quickly deactivate the catalyst. The higher yield of fuel hydrocarbons can be obtain through the deoxygenation of palmitic acids over 20wt% Ni/Al$_2$o$_3$ in presence of atmospheric mixture 50/150 H$_2$/N$_2$ which the presence of a small quantity of H$_2$ in inert gas keep the catalytic activity for a long time and decrease the amounts of unsaturated hydrocarbons and aromatics leading to coke formation. [27] The total conversion of carboxylic group in the palmitic acid is 69.1%as shown in table (2). It is clear that about 26.02% of isomers and olefin appears among the reaction products in case of using H$_2$/N$_2$ as atmosphere pressure mixture as shown in table (2) and gas chromatographic analysis (GC) as shown in Figs(4,5,6). This value decreases to 3.24% in presence of pure hydrogen pressure. This is due to that at pure hydrogen pressure the olefins hydrogenated to the corresponding paraffins. Additionally the n-hexadecane formed by direct hydrodeoxygenation reaction in a small amount approximately (<2%) over Ni catalysts.[28]

Table (2) Deoxygenation reactions of palmitic acid using 20wt%Ni/Al$_2$O$_3$ in the presence of different atmosphere.

Reaction	nC$_{15}$	Isomers and olefins	Fatty acid After reaction	Dimer	nC$_{16}$	Total conversion%	Selectivity to nC$_{15}$ %
20wt%Ni/Al$_2$O$_3$ 300^{0}C-6hs-50psiH$_2$+150psiN$_2$	41.48	26.01	30.94	1.30	0.20	69.06	60.21
20wt%Ni/Al$_2$O$_3$ 300^{0}C-6hs-200psi H$_2$	18.22	3.24	71.65	6.12	0.75	28.35	64.30
20wt%Ni/Al$_2$O$_3$ 300^{0}C 6hs-200psi N$_2$	6.98	10.55	78.51	3.78	0.13	21.49	32.49
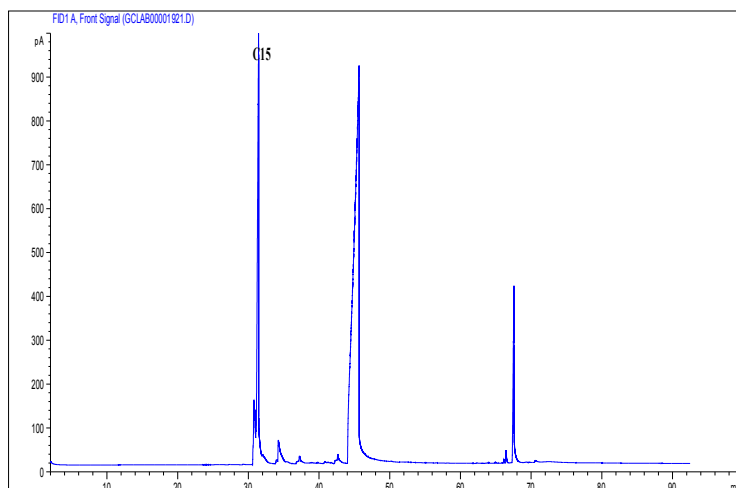
Fig(4) GC chromatograme of reaction of palmitic acid at 300c^o, pure H$_2$ for 6hs by using 20wt%Ni/Al$_2$O$_3$.
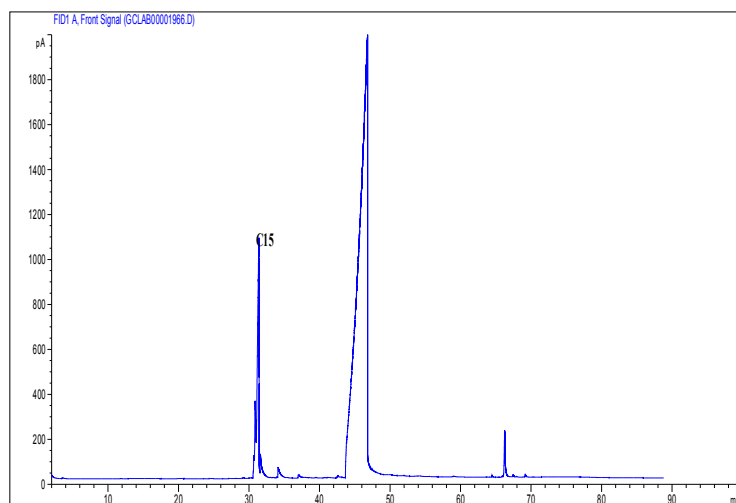
Fig (5)GC chromatograme of reaction of palmitic acid at 300c^o, pure N$_2$ for 6h by using 20wt%Ni/Al$_2$O$_3$.
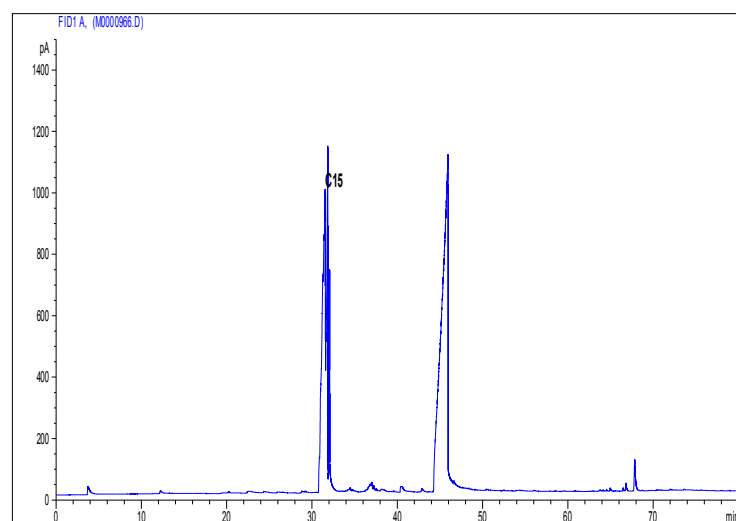
Fig.(6) GC chromatogram of palmitic acid in the presence of 20 wt% Ni/Al$_2$O$_3$ at 300C^0 under mixture of H$_2$ and N$_2$ for 6hs
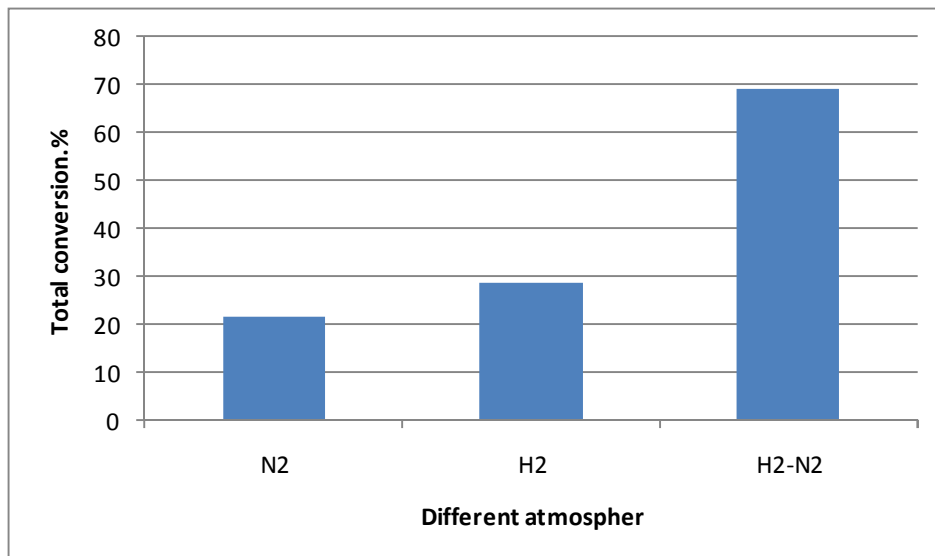
Fig.(7) Total conversion at different atmosphere in the presence of 20 wt% Ni/Al$_2$O$_3$ catalyst.
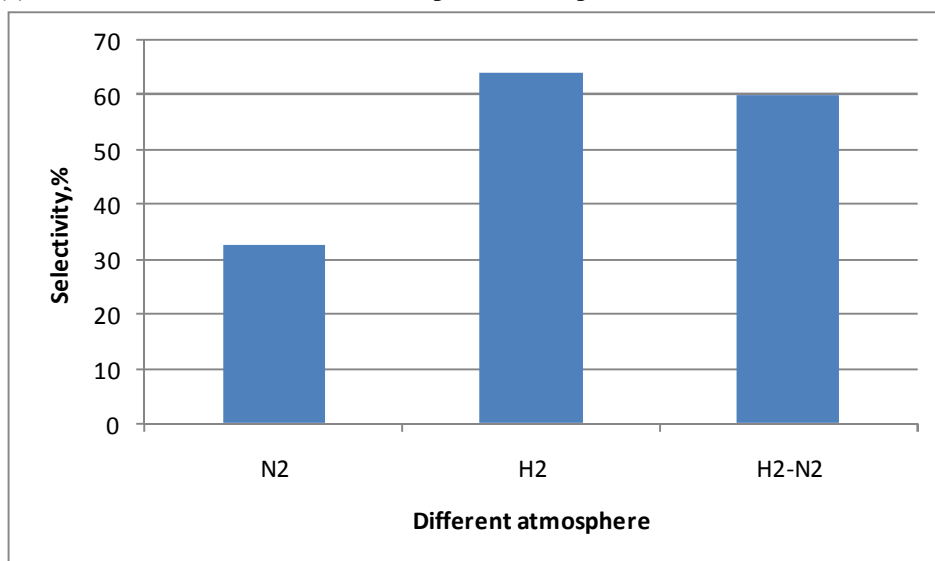

Fig.(8) Selectivity for C$_{15}$ at different atmosphere in the presence of 20 wt% Ni/Al$_2$O$_3$ catalyst.

**3-2-2 Effect of temperature on the deoxygenation process.**

The deoxygenation reaction of 10gm pure palmitic acid to diesel like hydrocarbon (green diesel) over 1g 20wt%Ni/Al$_2$O$_3$ catalyst in 200ml n- hexane at different temperatures 300^{0}C,325^{0}C and 350^{0}C under atmospheric mixture of 50psiH$_2$/150psiN$_2$ for 6hs has been studied. The reaction products were detected and identified using gas chromatography. The results of analysis were represented in Table(3) and Figs(6,9,10). It can be noticed from Table (3) and Figs(6,9,10) that the reaction temperature has important effect on conversion and yield/selectivity of diesel-like hydrocarbon which as the temperature increases the yield of the products increases, while the

amount of palmitic acid decrease. [29] The total conversion increases from 69.06% to 99.61% by increase the temperature from 300^{0}C to 350^{0}C. The deoxygenation of palmitic acid over 20wt%Ni/Al$_2$O$_3$ catalyst indicated that the high selectivity for n-alkane (C$_{15}$) (60.21%) at 300^{0}C and reach maximum value (85.54%) at 325^{0}C. It is clear that the yield of n-alkanes at 325^{0}C (90.52%) is higher as compared with that of isomers and olefins (7.35) as shown in table (3) and Figs (11, 12). This means that the deoxygenation through decarboxylation was more intense than that through decarbonylation. The heavy product formed over nickel catalysts may be due to extent of cracking and subsequent olefin metathesis to dimers.[30]

Table (3) Deoxygenation reactions of palmitic acid using 20wt%Ni/Al$_2$O$_3$ in the presence of different temperature

Reaction	nC$_{15}$	Isomers and olefins	Fatty acid after reaction	Dimer	nC$_{16}$	TotalConversion %	Selectivity for C$_{15\%}$
300^{0}C 20wt%NI/Al$_2$o$_3$-6hs-50psiH$_2$+150psiN$_2$	41.48	26.01	30.94	1.30	0.20	69.06	60.21
325^{0}C20wt%Ni/Al$_2$o$_3$-6hs-50psiH$_2$+150psiN$_2$	84.46	7.35	1.27	0.68	6.07	98.73	85.54
350^{0}C20wt%Ni/Al$_2$o$_3$-6hs50psiH$_2$+150psiN$_2$	52.46	43.60	0.39	0.81	2.71	99.61	52.67
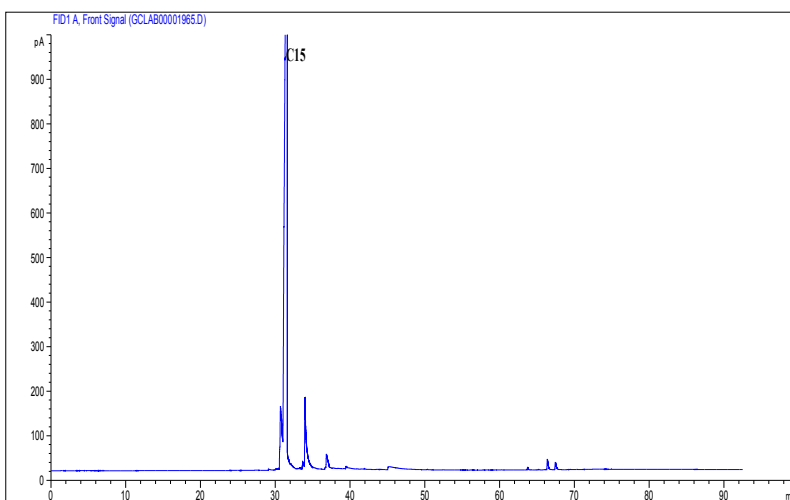
Fig.(9) GC chromatogram of palmitic acid in the presence of 20 wt% Ni/Al$_2$O$_3$ at 325C^0 unde mixture of H$_2$ and N$_2$ for 6hs.
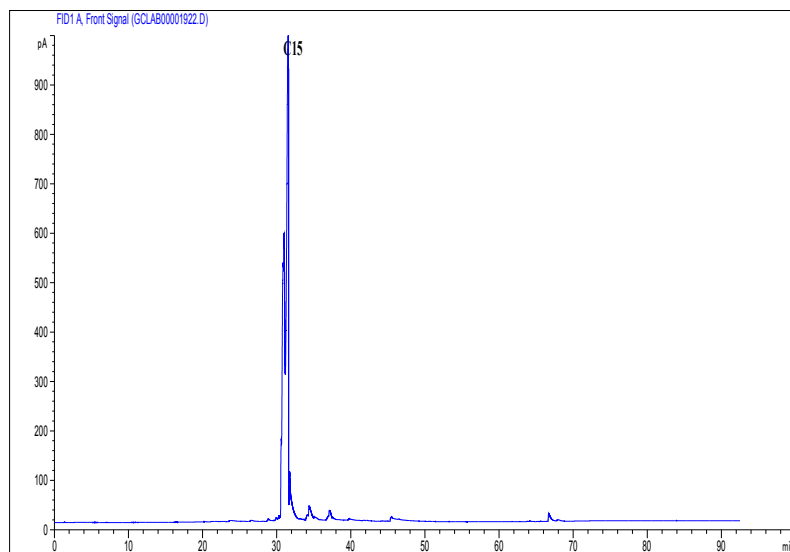
Fig.(10) GC chromatogram of palmitic acid in the presence of 20 wt% Ni/Al$_2$O$_3$ at 350C^0 under mixture of H$_2$ and N$_2$ for 6hs.
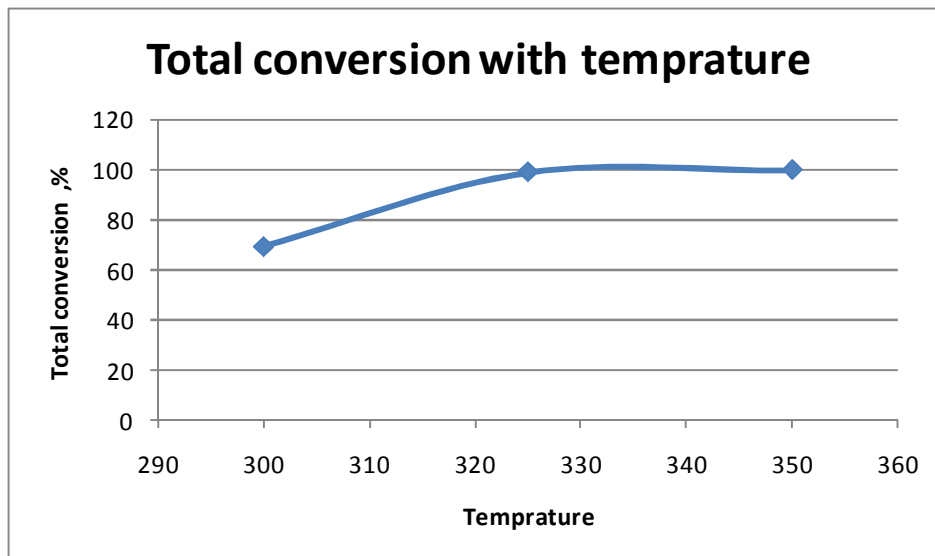
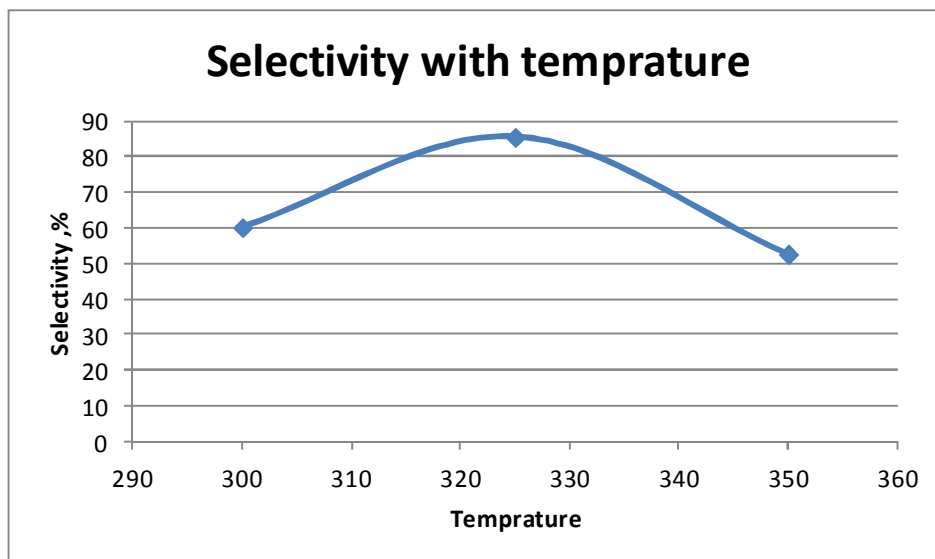**Fig (11) Effect of temperature on the total conversion using 20wt%Ni/Al₂O₃ catalyst.**

Fig (12) Effect of temperature on the selectivity using 20wt%Ni/Al₂O₃ catalyst

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