



Recent trends for clean fuel production by deoxygenation of pure palmitic acid using Ni/C catalyst



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Abstract

Deoxygenation of triglycerides is one of key processes making possible a convenient production of high quality automotive fuels components (sulfur-, oxygen- and aromatics-free). This reaction was studied over non noble metal catalysts 20wt%Ni/C and performed in batch reactor system (autoclave) by using pure palmitic acid, n-hexane as a solvent and 200 psi pressure. The effect of different atmospheres (pure hydrogen, pure nitrogen, and mixture of 50 psi H₂/150psiN₂) and different temperature range (300 °C-350 °C) under a mixed atmosphere (50 psiH₂/150psi N₂) were studied in this paper.

The main product was n-pentadecane (C₁₅) which the catalyst Ni/C has lower cracking selectivity to light hydrocarbons. The total conversion of carboxylic groups of palmitic acid and the selectivity to C₁₅ in case of pure nitrogen are (22.29% and 12.38%) respectively and in case of hydrogen they are (75.16% and 80.07%) respectively. In case of using H₂/N₂ as a mixture the total conversion and the selectivity are (81.18% and 75.32%) respectively for Ni/C catalyst. The total conversion increases from 81.18% to 99.99% by increase the temperature from 300 °C to 350 °C. The deoxygenation of palmitic acid over 20wt%Ni/C catalyst indicated that the high selectivity for n-alkane (C₁₅) (75.32%) at 300 °C and reach maximum value (98.11%) at 350 °C. Analysis of liquid products by gas chromatography (GC) was used to determine n-alkane (C₁₅) yield and other products (isomeres, olefins and dimers). Insights pertaining to the reaction scheme and an assessment of the reaction products as liquid transportation fuels are also provided in this contribution.

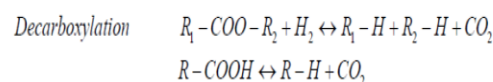
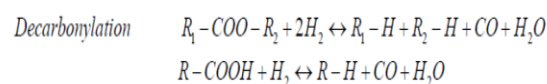
Keywords: Fatty acids; Catalytic Deoxygenation; Ni catalysts; Green Diesel

1. Introduction

Deoxygenation of triglycerides is one of key processes making possible a convenient production of high quality automotive fuels components (sulfur-, oxygen- and aromatics-free). Various alter-native routes for upgrading of triglycerides and related feedstocks, such as free fatty acids, into hydrocarbons have been reported in the literature [1–3].

Hydrodeoxygenation (HDO) includes mainly three reaction mechanisms. They are decarbonylation (DCN), decarboxylation (DCX), and reductive deoxygenation without C–C cleavage (RDO). The process of reductive deoxygenation (RDO) is quite different from the other two reaction mechanisms.

The main difference is that in case of RDO, all oxygen atoms in the organic acid are removed in the form of water requiring a substantial amount of hydrogen, while in the DCN and DCX mechanism most of the oxygen is removed in the form of CO₂ and CO. [4-5].



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Receive Date: 28 August 2020, Revise Date: 30 September 2020, Accept Date: 04 October 2020

DOI: 10.21608/EJCHEM.2020.40845.2829

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Murzin and co-workers have reported the results of detailed studies dealing with the metal-catalyzed deoxygenation of fatty acids over a variety of catalysts, and have extended this work to include fatty acid methyl and ethyl esters [6:13]. Notably, these authors found palladium supported on activated carbon to display the most promising catalytic performance in these reactions. In addition, Immer et al. have described the deoxygenation of C₁₈ fatty acids over Pd/C [14], while Do et al. have reported that the deoxygenation of fatty acid methyl esters can also be effectively catalyzed by Pt/Al₂O₃ [15]. However, considering the high cost of noble metals, the development of more affordable catalysts showing similar performance and durability is of great interest from an industrial standpoint. Recently, we have shown that Ni-based catalysts are highly active for the upgrading of soybean oil and model triglycerides in batch reactors [16,17], while Lercher and co-workers have demonstrated that Ni-containing bifunctional catalysts can be employed to convert algal lipids to diesel-range alkanes in both batch and continuous mode [18].

The deoxygenation process of palmitic acid was carried out at different temperatures (300 °C, 325 °C and 350 °C) in n-hexane solvent under a mixed atmosphere (50psiH₂/150psiN₂) flow for 6h. It is found that the reaction temperature affected conversion, yield and selectivity to diesel like hydrocarbon, which the total conversion of palmitic acid increases from (69.05% to 99.60%) and from (81.20% to 99.99%) by increasing the temperature from 300 °C to 350 °C in presence of Ni/Al₂O₃ and Ni/C catalyst respectively [6, 19].

In light of this, in this work 20 wt.% Ni/C was evaluated in the catalytic deoxygenation of fatty acids and used cooked oil in a semi-batch reactor and its performance compared to that of required gas (mixture of 50 psi H₂ / 150 psi N₂ -200 psi H₂ or 200 psi N₂) and heated to the temperature (300 °C-325 °C and 350 °C). Insights pertaining to the reaction scheme and an assessment of the reaction products as liquid transportation fuels are also provided in this contribution.

2. Experimental

2.1 Materials.

The materials used were, Ni(NO₃)₂.6H₂O (> 97% purity), HNO₃ acid 69 %, urea, olive stones, H₃PO₄ acid (85%), palmitic acid, used cooked oil, n-hexane and deionized water. The raw material is olive stones as a waste from any olive factory residue. Olive stones from this olive residue were collected as follows: the dried olive stones firstly stirred with hot

water at 60 °C for several hours and then sieved to separate the olive stones from the unwanted material. The olive stones were finally dried at 100 °C overnight. The olive stone (OS) was directly impregnated with phosphoric acid. The ground and sieved olive stones were soaked with phosphoric acid (85 wt. %) in three different weight ratio as 1:1 (H₃PO₄: olive stone) at room temperature. The resultant mixture allowed to impregnation at room temperature for 4h with occasional stirring for achieving well penetration of chemical into the interior of the stone. Subsequently, the mixture dried at 105 °C overnight in vacuum oven. The impregnated sample was transferred to quartz tube (450 mm length and 40 mm diameter). The tube is placed inside a programmable electrical horizontal tubular furnace (Nabertherm, Labochem model R50/250/12). The sample was heated under continuous nitrogen flow (100 mL/min) at a rate of 10 °C/min from room temperature up to 600 °C for 3h at this temperature. The carbonized sample was cooled to room temperature under nitrogen flow. The produced activated sample was ground, sieved, and washed with deionized water several times until a pH = 6–7. The washed sample was dried at 110 °C and stored for characterization and adsorption studies.

The AC support was functionalized with nickel using a deposition-precipitation method.

In this procedure, 250 mL of an aqueous solution containing 15.286 g of Ni (NO₃)₂.6H₂O and 0.3 mL of HNO₃ 69 % 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 12.281 g of the AC support to make a suspension. The suspension was heated at 40 °C, and then mixed with the urea solution under continuous stirring. After that, the mixture was heated to 90 °C for 8h under static condition then ageing 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 24h. After drying the sample Ni/C was heated in muffle at 300 °C for 6h to decompose the metal salt. Then this sample was reduced in tube furnace at 350 °C for 3h under hydrogen stream by ramp (5 °C/min), and then cooled to room temperature then put in a desiccator. We used methanolic Ni (NO₃)₂.6H₂O as the metal precursor for wet impregnation of Ni on the activated carbon.

2.2 Catalyst characterization

X-ray diffraction analysis was performed on the prepared activated carbons to determine the degree of crystalline or amorphous nature of the ACs. The

analyses were performed by A Philips PANalytical X'pert PRO diffractometer. X-ray patterns were taken by the thin powder sample was placed onto an oriented monocrystalline quartz plate for exposure to a Cu K α X-ray source ($\lambda = 1.5406 \text{ \AA}$) radiation source operating at the voltage of 40 KV and a current of 40 mA with Ni-filtered radiation.

The textural properties (surface area, pore volume, pore diameter and pore size distribution) of the catalysts studied were determined via N₂ physisorption. Catalyst samples were repeatedly outgassed at 200 °C for 90 min and analyzed until repeat analyses agreed and the measured sample mass after outgassing was no longer decreasing. The specific surface areas (SBET, m²g⁻¹) of the samples were calculated according to the Brunauer, Emmett and Teller (BET) method. Pore size distributions of the samples were determined from the desorption branch of the isotherms using the Barrett–Joyner–Hallenda (BJH) method.

FTIR spectroscopy was performed on the supports (AC) and catalysts (Ni/C) in order to obtain detailed information about the molecular structure of the catalysts. FTIR spectroscopy for the test materials was carried out by Fourier transform infrared spectrometer; Varian (Model: FTS-800) FTIR in the range 4000–400 cm⁻¹.

The Determination of acidity of the catalysts (Ni/C) was performed by using pH meter according to standard test method. The morphology of nickel particles on activated carbon supports is studied by TEM.

2.3 Deoxygenation experiments.

The deoxygenation experiments were carried on model fatty acid such as palmitic acid and used cooking oil by using batch reactor. Palmitic acid is a saturated fatty acid with formula C₁₆H₃₂O₂, 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.

Experiments were performed in a mechanically stirred 100 mL stainless steel autoclave operated in semi-batch mode. Typically, the catalyst (0.5 g) in powder form (particle size <150 μm) was reduced in situ under flowing 10% H₂/N₂ for 3h (at 350 °C for Ni/C) prior to purging the reactor with Ar and adding both solvent (hexane, 25 g) and feedstock (1.75 g). The autoclave was then purged three times with Ar prior to being pressurized with the required gas (N₂, 10% H₂/N₂ or H₂) and heated to the reaction temperature. The system was kept at 300 °C and 135psi for 1.5h. The autoclave temperature was measured by a type-K Omega thermocouple placed inside the reactor body. The reactions were performed under constant gas flow of 70 mL/min and 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 and most of the uncondensed gases were vented, albeit gas samples were taken and analyzed at representative intervals throughout the duration of the experiments.

Although the gas chromatograms of these samples showed the presence of small peaks corresponding to CO₂, CO and C₁–C₆ hydrocarbons, the quantification of these analytes was made impossible by the interference of the considerably larger GC peaks corresponding to H₂ and/or N₂, which were present in great excess and tended to flood the detector. At the completion of each test, forced air was used to facilitate cooling. Once the reactor reached room temperature, oil and catalyst were removed from the reactor and separated by gravity filtration to isolate the products. The recovered solids were then extracted twice with chloroform to yield additional material. Mass balances were typically greater than 90%, losses being mainly attributed to the formation of gaseous products which could not be accurately quantified (and which therefore were not factored into the mass balance calculation).

The waste oil sample was deoxygenated under a mixture atmosphere (50 psi H₂ /150 psi N₂) at 325 °C in the presence of catalyst (20wt%Ni/C) for 6h. Mass balances were typically greater than 90%, losses being mainly attributed to the formation of gaseous products which could not be accurately quantified (and which therefore were not factored into the mass balance calculation).

2.4 Product analysis.

Gas chromatography (GC Agilent 7890A) equipped with flame ionization detector (FID), mobile phase (carrier gas) was N₂ and HP-5 column (length 30 m, internal diameter 0.32 mm, film thickness 0.25 μm). The following temperature program was used for analysis: 50 °C (10 min) by ramp 4 °C /min to 300 °C (20min). Varian CP 3800 natural gas analyzer equipped with thermal conductivity detector (TCD), flame ionization detector (FID), porapak column (1/8 inch, 6feet), molecular sieve column (1/8 inch, 4feet) and DB-1 column (60m, 0.32mm, 5 μm). Mobile phase (carrier gas) was N₂ and He.

3. RESULTS AND DISCUSSION.

3.1 Catalyst Characterization.

3.1.1 X-ray diffraction (XRD).

The phase identity and crystallinity of the catalyst were revealed throughout the XRD patterns. Activated carbon produced from olive stones using phosphoric acid as activating agent can be crystallographically characterized by means of x-ray diffraction as shown in Fig. (1).

Fig. (1-a) illustrates the x-ray diffraction (XRD) pattern of the activated carbon. Appearance of broad diffraction background and the absence of a sharp peak reveals a predominantly amorphous structure. There are two broad diffraction peaks corresponding to 2θ around 240 and 430 in the spectrum. The crystallinity registered olive stone is contained a large grade of amorphous. The recorded value was identical with the values in literature that used different lignocellulosic raw material [20].

The presence of broad peaks at these 2θ in assigned to an increasing regularity of crystal structure and resulting in better layer alignment [21].

Fig (1-b) shows the x-ray diffraction patterns of nickel supported on activated carbon. The noted peak at 2θ 240 ascribed to the reflection of amorphous carbon (support) [00-002-0456]. Apart from the characteristic peaks of carbon support, the peaks at 44.50, 51.90 and 74.60 can be assigned to Ni [03-065-0380].

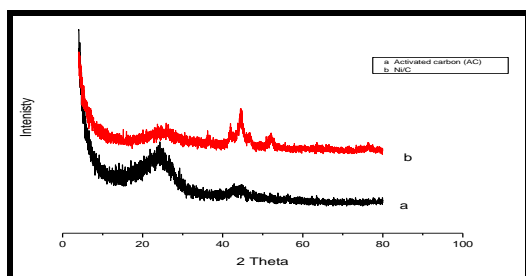


Fig.1 : XRD of a- Activated carbon (AC) , b- Ni/C

3.1.2 FTIR-spectroscopy .

The carbon matrix does not consist of carbon atoms alone, but also is formed by other heteroatoms like hydrogen, oxygen, halogen, sulfur, phosphorus, etc. These heteroatoms are bonded to the edges of the carbon layers, which is governing the surface chemistry of the activated carbon. FTIR spectrum of activated carbon obtained from olive stone activated by phosphoric acid (as activating agent) is shown in Fig(2). The spectrum shows broad absorption band around 3600-3200 cm^{-1} with a maximum peak at 3422 cm^{-1} . This band may be assigned to the O-H stretching mode of hydroxyl groups and adsorbed water. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds (from carboxyls, phenols or alcohols). The FTIR spectrum of activated carbon shows absorption bands at 2922 cm^{-1} , 2852 cm^{-1} due to aliphatic unit as symmetric and asymmetric stretching in C-H, CH_2 or CH_3 bonds and 1459 cm^{-1} band shows -CH- deformation. The small peak around 1700 cm^{-1} shows the presence of stretching vibrations of C=O in ketones, aldehydes, lactones or carboxyl groups. The bands between 1600 and 1400 cm^{-1} are usually ascribed to C=C vibration in the

aromatic ring. There is also a presence of broad band between 1300-1000 cm^{-1} with a strong band at 1100 cm^{-1} is usually found with oxidized carbons and has been assigned to C-O stretching in acids, alcohols, phenols, ethers or esters groups. Nevertheless, it is also a characteristic band for phosphorus and phosphor carbonaceous compounds (e.g phosphates and phosphoric acid esters) present in the phosphoric acid activated carbons. The small band at 789 cm^{-1} is due to out of plane deformation mode of C-H for different substituted benzene rings [22].

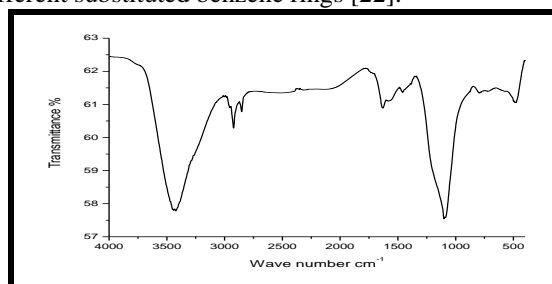


Fig.2 : FTIR spectrum of activated carbon

3.1.3 Surface area.

The surface area, pore size distribution and pore volume of activated carbon and nickel supported activated carbon (20wt%Ni /C) are shown in Table (1).

The surface 1203.68 m^2/g was observed for activated carbon, while that of the nickel supported catalyst revealed 865.8 m^2/g as observed from the Table (1), the surface area of the supported catalyst was slightly less than that of pure support due to increasing nickel loading on activated carbon. This may be due to coverage of surface area of activated carbon and blockage of pores by nickel or nickel oxide [23]. So that, the total pore volume decreased from 0.99 to 0.75 ml/g for activated carbon and 20wt%Ni/C catalyst. In case of activated carbon the carbonization temperature and phosphoric acid concentration can effect on BET surface area, pore size and total pore volume. The increase in porosity with temperature can be attributed to the release of tars from cross linked frame work generated by the treatment of phosphoric acid [24]. The pH of 20wt%Ni/C catalysts is (5.7). 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]

Table 1: The surface area, pore size and pore volume of activated carbon and nickel supported activated

Catalyst	Surface area m ² /g	Average pore size nm	Total pore volume ml/g
Activated carbon	1203.68	3.29	0.99
20 wt %Ni/C	865.8	3.46	0.75

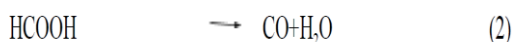
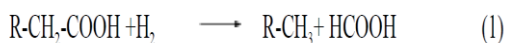
3.1.4 Transmission Electron Microscopy (TEM).

The morphology of activated carbon and Ni supported on activated carbon are shown in Fig.3. The typical TEM image for activated carbon in Fig.(3-a) shows that the particles of activated carbon were agglomerated to form a wide size distribution with size range of 11.4-19.9nm. Whereas the TEM image of nickel particles supported on activated carbon in Fig.(3-b) demonstrated that the metal particles are dispersed as aggregate clusters located entirely on the activated carbon surface with particle size distribution in the range 2.2-5.4 nm. The TEM micrograph illustrated that the nickel loading does not lead to agglomeration of the particles which may indicate strong metal support interaction and hence a high degree of dispersion on activated carbon ensuring in turn a high degree of conversion. This structural property affects the catalytic performance [26].

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

The deoxygenation of palmitic acid were performed over 20 wt% Ni/C under three different atmospheres namely pure nitrogen, 50/150 hydrogen/nitrogen mixed atmosphere and pure hydrogen at 300 °C for 6h have been studied. The results were represented in Table (2). The results in Table (2) indicated that the total conversion of carboxylic groups of palmitic acid and the selectivity to C₁₅ in case of pure nitrogen are (22.29% and 12.38%) respectively and in case of hydrogen they are (75.16% and 80.07%) respectively. In case of using H₂/N₂ as a mixture the total conversion and the selectivity are (81.18% and 75.32%) respectively for Ni/C catalyst. It is clear that the total conversion of carboxylic group and selectivity of C₁₅ is lower in the presence of pure nitrogen than that in case of pure hydrogen. 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 [27] as the following equations.



Carbon monoxide produced may be adsorbed on the catalyst surface before it can be removed from the system and inhibiting the deoxygenation process 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 obtained through the deoxygenation of palmitic acids over 20wt% Ni/C catalyst in presence of atmospheric mixture 50/150 H₂/N₂ which the presence of a small amount of H₂ in inert gas keep the catalytic activity for a long time and decrease the amounts of unsaturated hydrocarbons and aromatics leading to coke formation. [28]

It is noticed amount of isomers and olefin appears among the reaction products as shown in Table (2) and gas chromatographic analysis (GC) as shown in Figs(4,5,6). Additionally the n-hexadecane formed by direct hydrodeoxygenation reaction in a small amount approximately (<2%) over Ni catalysts. [29]

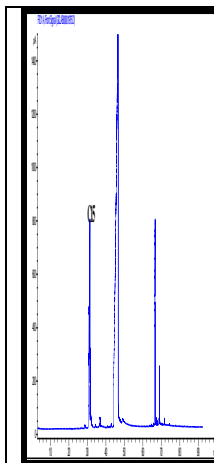


Fig. 4: GC chromatogram of palmitic acid in the presence of 20wt% Ni/C At 300°C under pure N₂.

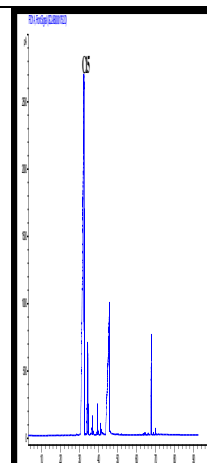


Fig. 5: GC chromatogram of palmitic acid in the presence of 20wt% Ni/C At 300°C under pure H₂.

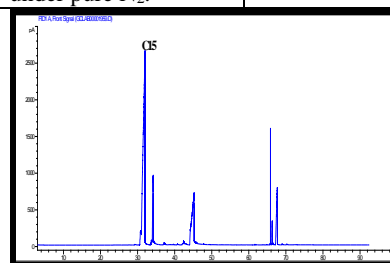


Fig. 6: GC chromatogram of palmitic acid in the presence of 20wt% Ni/C at 300°C under mixture of H₂ and N₂.

Table 2: Deoxygenation reactions of palmitic acid using 20wt%Ni/C in the presence of different atmospheres.

Reaction	nC15 wt%	Isomers, olefins wt%	Fatty acid After reaction wt%	Dimer wt%	C16 wt%	Total conversion %	Selectivity to nC15 %
20 wt%Ni/C,300 ⁰ C-6hs50psiH ₂ +150psiN ₂	61.3	2.54	18.82	10.47	7.01	81.18	75.32
20 wt %Ni/C, 300 ⁰ C-6hs, 200 PsiH ₂	60.18	5.13	24.84	5.52	4.31	75.16	80.07
20 wt %Ni/C, 300 ⁰ C-6hs, 200 psi N ₂	2.76	10.86	77.71	8.55	0.10	22.29	12.38

Table 3: Deoxygenation reactions of palmitic acid using 20wt%Ni/C in the presence of different temperatures.

Reaction	nC15 wt%	Isomers, olefins wt%	Fatty acid After reaction wt%	Dimer wt%	C16 wt%	Total conversion %	Selectivity to nC15 %
3000C 20 wt%Ni/C-6hs 50psiH ₂ +150psiN ₂	61.13	2.54	18.82	10.47	7.01	81.18	75.32
3250C 20wt%Ni/C-6hs 50psiH ₂ +150psiN ₂	72.08	22.62	2.99	1.18	1.11	97.01	74.32
3500C 20wt%Ni/C-6hs 50psiH ₂ +150psiN ₂	98.11	0.66	0.0001	0.02	1.19	99.99	98.11

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

The deoxygenation reaction of 10 gm pure palmitic acid to diesel like hydrocarbon (green diesel) over 1g 20wtNi%C catalyst in 200ml n- hexane at different temperatures 300 °C, 325 °C and 350 °C under atmospheric mixture of 50psiH₂ /150psiN₂ for 6hs has been studied. The reaction products were detected and identified using gas chromatography. The results of analysis were represented in Table (3).

It can be noticed from Table (3) 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. [30] The total conversion increases from 81.18% to 99.99% by increase the temperature from 300 0C to 350 0C. The deoxygenation of palmitic acid over 20wt%Ni/C catalyst indicated that the high selectivity for n-alkane (C₁₅) (75.32%) at 300 °C and reach maximum value (98.11%) at 350 °C. It is clear that the yield of n-alkanes at 350 °C (99.30%) is higher as compared with that of isomers and olefins (0.66) as shown in Table (3) and Figs (7,8, 9).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 dimmers [31].

3.3 Deoxygenation of the used cooked oil sample.

3.3.1 Chemical composition of waste oil sample

Table (4) shows the summary of fatty acid content in the waste oil sample. From Gas chromatography analysis, it was found that the oil sample contains about (29.20%) of saturated fatty acids and (70.80%) of unsaturated fatty acids. The oil sample contains the highest amount of mono unsaturated acid (41.14%) among other fatty acids. Poly unsaturated fatty acids were found to be approximately (29.66%). The oil sample contains mainly (19.51%) stearic acid followed by (8.97%) palmitic acid.

3.3.2 Deoxygenation reaction of used cooked oil sample.

Catalytic deoxygenation of used cooked oil sample was studied over the catalyst (20wt%Ni/C) under atmosphere of mixture of (50psiH₂+150psiN₂) at temperature 325 °C in the presence of n-hexane solvent for 6hrs. The results of GC analysis were represented in Table (5) and Fig (10).

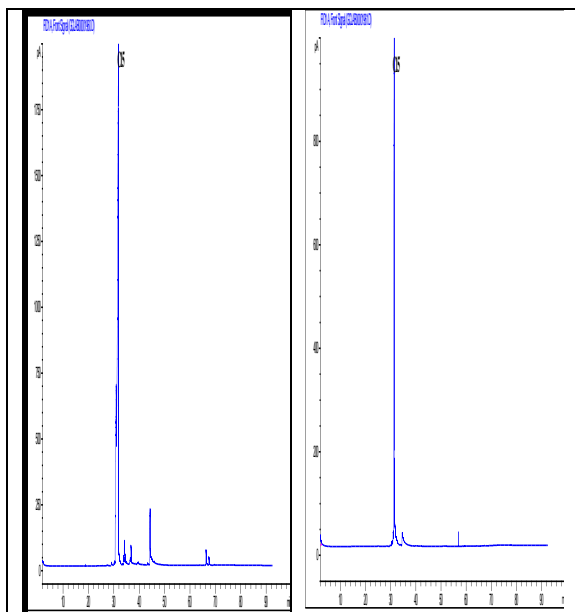


Fig. 7: GC chromatogram of palmitic acid in the presence of 20wt% Ni/C at 325°C under mixture of H₂ and N₂.

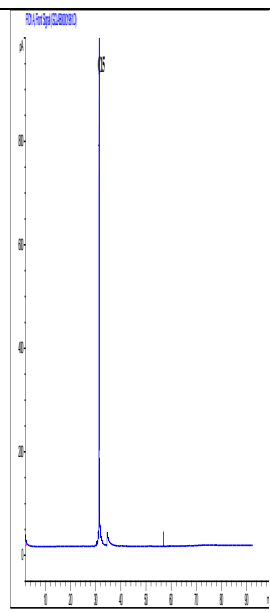


Fig. 8: GC chromatogram of palmitic acid in the presence of 20wt% Ni/C at 350°C under mixture of H₂ and N₂.

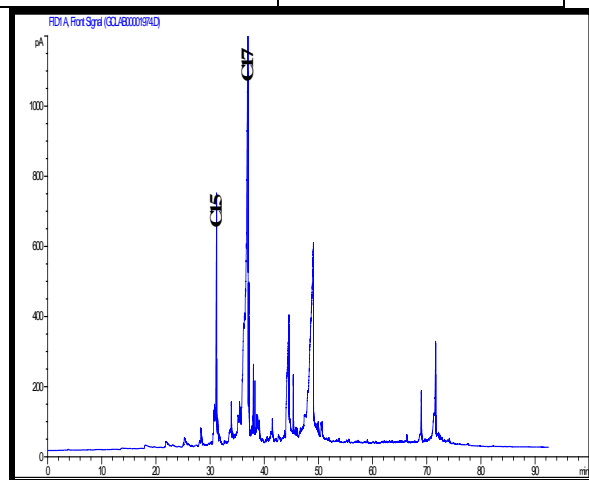


Fig. 9: GC chromatogram of waste oil sample in the presence of 20wt% Ni/C at 325°C under mixture of H₂ and N₂.

Table (4): The chemical composition of the used cooked oil sample.

Oil composition	Carbon chain	Wt%
Palmitic acid	C16:0	8.97
Palmitoleic	C16:1	5.70
Stearic acid	C18:0	19.51
Oleic acid	C18:1	35.44
Linoleic acid	C18:2	10.30
Linolenic acid	C18:3	19.36
Arachidic acid	C20:0	0.72

Table (5): Deoxygenation reactions of waste oil sample using 20wt% Ni/C in the presence of a mixed atmosphere at 325 °C (liquid products).

Reaction	Hydrocarbons C ₁₁ -C ₁₇ wt. %	Oil after reaction wt. %	Dimmer wt. %	Total conversion	Selectivity to hydrocarbons
Oil with Ni/C	60.44	35.23	4.41	64.77	93.31

3.3.3 Liquid products.

It is found that the liquid product fraction (C₁₁-C₁₇) is the main products. It is clear that the total conversion of oil sample is (64.77%) in the presence of Ni/C catalysts as shown in Table (5) and the yield of (C₁₁-C₁₇) hydrocarbons was (60.44%). The Ni/C catalyst appears a higher conversion and give high yield of hydrocarbons (C₁₁-C₁₇) this can be due to the higher surface area of Ni/C catalyst (865.8 m²/g) as given in Table (1) so that the, catalyst deactivation occurs slowly due to the higher surface area. Several reactions occurred in the liquid phase e.g. hydrogenation, dehydrogenation, cyclization, isomerization and deoxygenation. Poly unsaturated fatty acids hydrogenated to mono unsaturated and saturated fatty acid. Additionally isomerization (double bond migration) of oleic acid occurred prior to hydrogenation and deoxygenation. Hydrogenation, isomerization and finally deoxygenation trends were observed to produce hydrocarbons. The linear C₁₇ hydrocarbons were n-heptadecane as the main components. The selectivity of the desired products was higher in the presence of Ni/C catalyst (93.31%) as shown in Table (5). The presence of unconverted fatty acids after deoxygenation reaction is (35.23%) for Ni/C catalyst. This is due to deactivation of catalyst which the oil contains high degree of unsaturation.

3.3.4 Gaseous products.

The analysis of gaseous products after 4hs by using GC was represented in Table (6). The results in Table (6) indicate that CO gas is the primary product. It is evident that 20wt% Ni/C catalyst gave higher yields of CO gas product (96.02%). This is due to the higher activity of the deoxygenation reaction. The tendency for formation of CO gas rather than CO₂ (0.52%) in presence of Ni/C catalyst as given in Table (6).

This is attributed to that the deoxygenation reaction of palmitic acid mainly via decarbonylation and it may be formed from CO₂ and H₂ as the following equation



Table (6): The gaseous products obtained by deoxygenation reaction of oil sample using the catalyst after 4h.

Gaseous products	20wt%Ni/C Mol.%
H ₂	0.000
CO	96.020
CO ₂	0.521
O ₂	1.947
CH ₄	1.440
C ₂ H ₆	0.011
C ₃ H ₈	0.003
ΣC ₄ +	0.058

The deoxygenation of palmitic acid was found to remove the carboxylic group in the fatty acid structure as CO and CO₂ gases and cracking the fatty acid chains producing liquid fuel like hydrocarbons Fig(10). The results in Table (6) indicate that the sum of CO and CO₂ gases (96.54%) over 20wt% Ni/C catalyst. It is evident that 20wt% Ni/C catalyst is the most active catalyst for Palmitic deoxygenation. The heavy product formed over nickel catalysts may be due to extent of cracking and subsequent olefin metathesis to dimmers

In the end, pentadecane and small amount of hexadecane were yielded as the final deoxygenation products. Pentadecane (C₁₅) was significantly more dominant than hexadecane (C₁₆). Unsaturated hydrocarbons were not detected at all. The concentration of palmitic acid and hexadecanol initially increased and then gradually decreased, indicating their nature as reaction intermediates. Moreover, palmitic acid appeared to be the primary intermediate, which is far more abundant than hexadecanol. Light gases (CH₄, CO and CO₂) were detected in the gas phase. Solvent cracking reaction was not observed until reaching full conversion of the oxygenated compounds (i.e. methyl palmitate and palmitic acid) only at 300 °C. Based on the product results, we can deduce the HDO reaction pathways of methyl palmitate over Rh/ZrO₂ catalyst, as shown in Fig. 10. The initial step is the hydrogenolysis of methyl palmitate, producing palmitic acid and gaseous CH₄. Palmitic acid can be further hydrogenated into hexadecanol via the removal of water, followed by decarbonylation reaction into pentadecane and CO. Meanwhile, hexadecanol was yielded via the hydrogenation of hexadecanal. Meanwhile, hexadecanol can be reversibly transformed to hexadecanal via its dehydrogenation. These routes can be further confirmed in separate experiments using palmitic acid or hexadecanol as reactant. Moreover, the water-gas-shift (WGS) and methanation reactions may have occurred, affecting the concentration of CO and CO₂ in the gas phase.

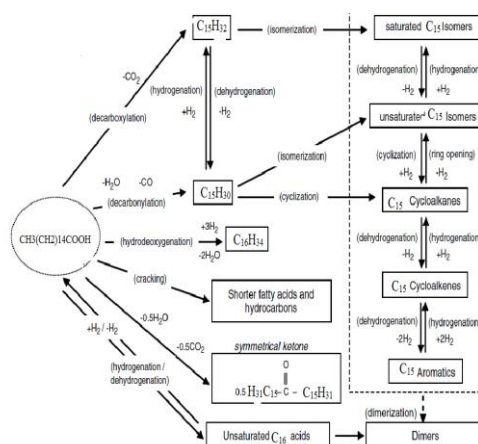


Fig 10: A simplified scheme shows the deoxygenation reaction of Palmitic acid

Even in the HDO of hexadecanol, the yield of hexadecane formed was less than 2.0% at almost complete conversion. It demonstrated that the dehydration reaction of hexadecanol was highly suppressed over Rh/ZrO₂ catalyst, whereas this route is remarkable over traditional sulfided NiMo/Al₂O₃ catalyst [6, 32].

4. Conclusions

In this work, we study the deoxygenation reaction (decarbonylation/decarboxylation) on palmitic acid under three different atmospheres, namely pure hydrogen, pure nitrogen and 50psiH₂/150psiN₂ mixture at 300°C for 6 hours and using n-hexane as a solvent. It is found that the total conversion of carboxylic group in palmitic acid is higher in presence of pure hydrogen as compared with that in case of pure nitrogen and the total conversion of palmitic acid by deoxygenation reaction increased to (81.17%) in presence of 20wt% Ni/C catalysts respectively, when replaced of pure hydrogen atmosphere with a mixture atmosphere containing 50psiH₂/150psiN₂ was used. Ni catalysts play an important role in the hydrogenation pathways. The selectivity and the activity of Ni-based catalyst can be enhanced with metal loading in combination with different supports.

5. Conflicts of interest

"There are no conflicts to declare".

6. References

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