

DEOXYGENATION OF PLANT FATTY ACID USING NiSnK/SiO₂ AS CATALYST

(Penyahoksigenan Asid Lemak Tumbuhan Dengan Menggunakan NiSnK/SiO₂ Sebagai Pemangkin Komposit)

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Abstract

Environmental friendly bio-oil which offers supply reliability as a potential alternative fuel, has spurred to rapid development of biofuels technology. Palm oil is a potential renewable energy source for biofuels production in the future and Malaysia is one of the world largest palm oil producers. However, undesired oxygen content in the plant fatty acid that contributes to low energy density, high viscosity, and low stability, makes the palm oil not effective to be used as biofuels directly. In the present study, the performance of silica supported trimetal catalyst, NiSnK/SiO₂, on deoxygenation of used palm oil was evaluated. In addition, the effects of operating parameters, such as reaction temperature and weight hourly space velocity were investigated. Conversion of palmitic acid as high as 90% was achieved in deoxygenation of used palm oil at reaction temperature 350°C. In order to have a better understanding on the deoxygenation reaction, model compound system using the major saturated fatty acid in the used palm oil, palmitic acid was also carried out. Palmitic acid was found mainly decarboxylated into n-pentadecane with some decarbonylation and isomerizations products.

Keywords: Deoxygenation, used palm oil, palmitic acid, NiSnK/Silica

Abstrak

Minyak-bio mesra alam yang menawarkan kebolehpercayaan bekalan sebagai bahan api alternatif yang berpotensi, telah membawa perkembangan pesat dalam teknologi bahan-api-bio. Minyak kelapa sawit adalah sumber tenaga boleh diperbaharui yang berpotensi bagi pengeluaran bahan-api-bio pada masa akan datang, dan Malaysia merupakan salah satu pengeluar minyak sawit yang terbesar di dunia. Namun, kandungan oksigen dalam asid lemak tumbuhan yang tidak diingini menyumbang kepada ketumpatan tenaga yang rendah, kelikatan yang tinggi, dan kestabilan yang rendah, menjadikan minyak sawit tidak berkesan untuk digunakan sebagai bahan api secara langsung. Dalam kajian ini, prestasi pemangkin, NiSnK/SiO₂ untuk penyahoksigenan minyak kelapa sawit dinilai. Di samping itu, kesan parameter operasi, seperti suhu tindak balas dan halaju ruang berat setiap jam (WHSV) telah dikaji. Penukaran asid palmitik setinggi 90% telah dicapai apabila penyahoksigenan minyak kelapa sawit dijalankan pada suhu tindak balas, 350°C. Untuk mendapatkan pemahaman lanjut mengenai tindak balas penyahoksigenan, sistem sebatian model menggunakan asid lemak tepu utama dalam minyak kelapa sawit terguna, asid palmitik, telah dijalankan. Asid palmitik didapati dinyahkarbosilan terutamanya kepada n-pentadekana dan beberapa produk penyahkarbonilan dan pengisomeran.

Kata kunci: Penyahoksigenan, minyak kelapa sawit terguna, asid palmitik, NiSnK/Silika

Introduction

Biofuels are renewable energy derived from biological carbon fixation, predominantly produced from biomass, which can be used as a substitute for depleting petroleum fuels. Natural plants and animals fats are promising source as fuel owing to their energy contents of the carbon chain. Biofuels refers to solid biomass (bio-char), liquid fuels (bioethanol, vegetable oil and biodiesel) or various gaseous (biogas, biosyngas, and biohydrogen) [1]. From energy security standpoint, utilization of biofuels displaces significant amounts of fossil fuels, and offers supply reliability. In terms of climate change mitigation, environmental friendly and biodegradable biofuels are attractive to reduce

greenhouse gas emissions, and hence reduce air pollution. For economic aspects, development of biofuels protects trade balances and promotes foreign exchange savings through reduce the dependency on imported petroleum. Biofuels create prospect of new economic opportunity for people in rural areas by increasing number of rural manufacturing and farming jobs [1-4].

Malaysia is the world's second largest palm oil producer, accounting for 42.3% of worldwide production. Furthermore, Malaysia is also world's largest palm oil exporter, accounting for 48.3% of world's total exports of palm oil [3]. The optimization of land usage for oil palm cultivation without deforestation has proven the sustainability of oil palm [4]. Thus, palm oil is most productive energy crops with abundant sources and hence a good candidates to enhance into excellent renewable energy in Malaysia [5]. Used cooking oil price is 2.5-3.5 times cheaper than virgin vegetable oils due to no market available for used cooking oil [1]. In order to avoid the fuel and food issue, used palm oil (UPO) is more suitable to be biofuels feedstock than edible palm oil.

However, the biofuels have oxygen levels from 10 to 45 percents. The undesired oxygen content produced especially insoluble impairs engine performance such as plugging of fuel filter, fouling of injector, sticking of ring, and formation of deposit in engine. Removal of oxygen contents inside plant fatty acid is required to improve biofuels quality; increase energy density, reduce viscosity, and stabilize biofuels [6-8]. Removal of carboxyl oxygen can be achieved via deoxygenation or hydrodeoxygenation. During reaction, hydrogen is consumed not only for hydrodeoxygenation, but also for side reaction such as methanation and water-gas shift reaction [9]. Therefore, hydrodeoxygenation is not economically applicable due to high consumption of excess hydrogen and hence high operating cost since raw material constitutes high percentage in expenses of a production line. Besides that, avoid utilization of hydrogen ensure a higher safety. Deoxygenation reactions of fatty acid in the absence of hydrogen flow can occur through two pathways, which are direct decarboxylation and decarbonylation. Direct decarboxylation removes carboxyl group and hence yields carbon dioxide and paraffinic hydrocarbon (alkane with one carbon atom less than original fatty acid), while direct decarbonylation yields carbon monoxide, water and olefinic hydrocarbon (alkene with one carbon atom less than original fatty acid) [10].

In 2006, Snåre et al. [11] evaluated a series of active metals supported on either aluminium oxide, silicon oxide, chromium oxide, magnesium oxide, or activated carbon as catalyst for deoxygenation of stearic acid to desired paraffin product, heptadecane. The comparison results of metal catalyst tested on similar supports by normalizing the metal content revealed the following order Pd>Pt>Ni>Rh>Ir>Ru>Os. In addition, 5% of palladium loading was reported to give the highest conversion of stearic acid and selectivity toward deoxygenated heptadecane. Later in 2008, 5 wt% Pd/C was reported deactivated due to coking and poisoning. Catalyst reactivation with hydrogen did not restore the catalyst activity [12].

Do et al. compared performance of 1 wt% platinum supported on gamma alumina (Pt/Al₂O₃) and titania (Pt/TiO₂) for deoxygenation of methyl octanoate and methyl stearate. The results showed that higher selectivity of heptadecane was achieved by utilization of Pt/Al₂O₃ as catalyst. Deactivation study was also carried out. Deactivation was reported due to oligomerization of unsaturated hydrocarbons and heavy compounds to coke which blocked the active site of catalysts [13]. Recently, catalytic deoxygenation of triglycerides to paraffins and olefins was carried out in a semibatch reactor with reactive distillation fashion, in which products were quickly removed from reaction mixture in flowing Helium. PtSnK/silica was found to be best catalyst for deoxygenation of triglycerides and methyl ester to olefins. Addition of tin was found to reduce sites that interact with hydrogen and CO strongly and consequently reduce selectivity to side reaction hydrogenation /hydrogenolysis by products [14].

Significant effect of tin addition on catalyst performance has reported before for linear olefin production from saturated fatty acid. The catalytic system consisted of nickel catalyst and at least a metal selected from the group consisting of tin, germanium or lead group. The nickel carrier preferably non-acidic silica, titanium oxide, or zinc oxide. NiSn catalyst achieved 65%, the highest selectivity to C₁₅ olefin, with no thermal cracking that resulted in product with less carbon number and hence low in energy density. Without tin addition, the olefin yield reduced to 6% only, and large fraction of cracking products produced [15].

Due to high cost of palladium and platinum catalyst, it is not suitable from economical view. A modified trimetal catalyst, NiSnK/SiO₂ for deoxygenation of plant fatty acid is being investigated in detail in the present study. The catalyst performance was evaluated over UPO and its model compound, palmitic acid.

Materials and Methods

Catalyst preparation

In this study, NiSnK/SiO₂ catalysts were prepared based on [14, 16]. SiO₂ support used was obtained commercially. Metal was loaded onto the support by incipient wetness impregnation method. The weight ratio of Ni:Sn:K was 1:1.3:1.5. Firstly, desired amount of nickel (II) nitrate hexahydrate, Ni (NO₃)₂·6H₂O (ACROS, 99%) and tin (II) chloride, SnCl₂·2H₂O (MERCK, 98%) were dissolved in distilled water, impregnated to silica support and followed by drying in air at 120°C for 16 hrs in oven [16]. Then, calcination was carried out in a muffle furnace at 700°C for 8 hrs. Potassium was then incorporated onto the prepared NiSn/SiO₂ catalyst with the same procedure by using KOH (MERCK, 85%) as the potassium precursor, but calcined for 2 hrs at 400°C in the air [14].

Catalyst characterization

Catalyst specific surface area, pore size and pore volume were measured by nitrogen adsorption-desorption at liquid nitrogen temperature using a Micrometrics ASAP 2020 System. Prior to the measurements, samples were degassed at 77 K for 4 hrs. Pore size distributions were obtained using Barrett-Joyner-Halenda (BJH) model applied to desorption isotherms data. The micropores area were estimated using the correlation of *t*-plot method [17].

X-ray diffraction (XRD) analysis was carried out by a Philips X-Ray Diffractometer. The diffraction patterns were recorded using Cu-K α radiation and taken in the range of 10-90° (2 θ).

Catalyst activity test

The deoxygenation reactions were conducted in a fixed-bed reactor with outer diameter of ½ inch. Schematic diagram of the reactor system is shown in Figure 1.

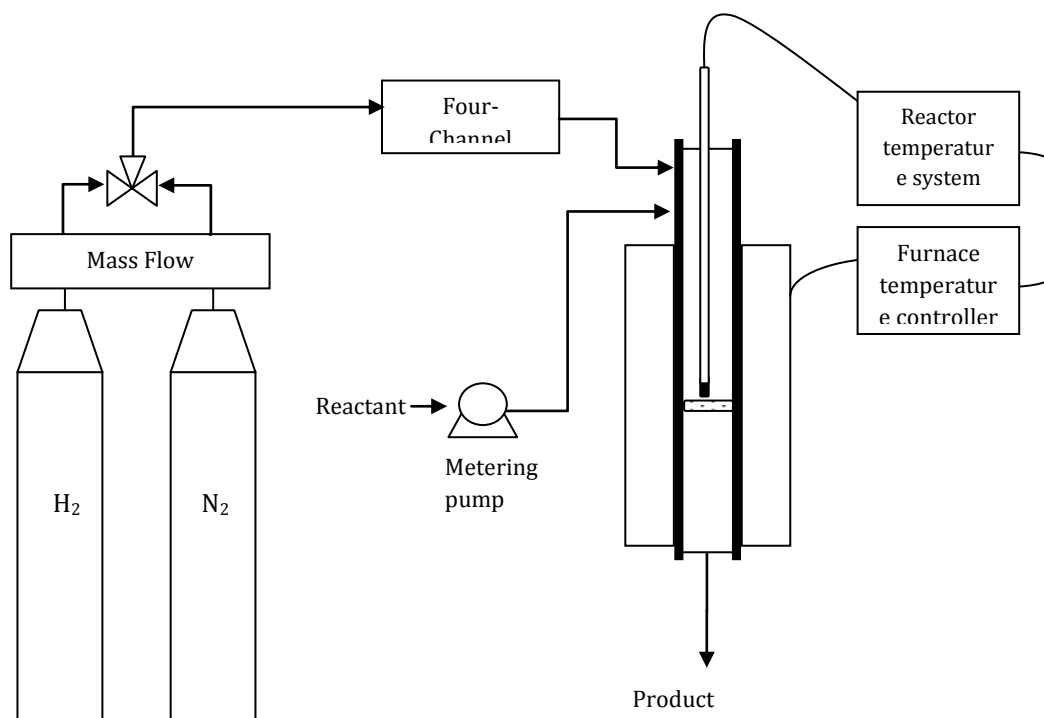


Figure 1. Schematic diagram of fixed-bed reactor system

Prior to reactions, the catalyst was activated based on [18], reduced in flowing H₂ (100cm³ (STP) min⁻¹) for 2 hrs at 200°C. Then, the reactor was replaced by 10 ml/min nitrogen flow. The flow of hydrogen and nitrogen gas was controlled by mass flow controller (MKS Instrument model M100B). The reactor was heated up to the desired temperatures in a tube furnace (Nabertherm B170).

When reaching desired temperature, feedstock (UPO without solvent, or palmitic acid dissolved in dodecane solvent) was pumped into the reactor from the top by using a metering pump. The feed rate was determined based on weight hourly space velocity (WHSV) of the reaction. Liquid sample from reactor outlet was collected in every half an hour interval continuously for 3 hours. The liquid product was analyzed by an offline gas chromatography (Perkin Elmer) equipped with a flame ionization detector (FID) and HP-INNOWAX capillary column (30m x 0.25mm x 0.25 µm).

Results and Discussion

Used Palm Oil (UPO)

The feed, UPO was analyzed by using a gas chromatograph-mass spectrometry (GC-MS). It showed that the major components were oleic acid and palmitic acid, which is in agreement with major components reported [19, 20], as shown in Table 1. Impurities of aldehyde (such as dodecanal, and 9-octadecanal) and alcohol (such as 2-methyl-1-hexadecanol and 1-heptadecanol) existed in small concentration have also been found in the current research. It is due to the presence of oxygen atoms in fatty acid which undergo oxidation into alcohol, aldehyde and insolubles. The degraded chains will polymerize and hook together into insoluble gums and hence cause clogging parts in engine if the oil is applied as engine fuel [21].

Table 1. Major composition of fatty acid in UPO (waste cooking oil) [20]

Fatty acid common name	Abbreviation*	Composition (wt %)
Palmitic acid	16:0	22.47
Stearic acid	18:0	12.51
Oleic acid	18:1	27.64
Linoleic acid	18:2	14.58

*Abbreviation was referred to number of carbon atoms: number of double bonds.

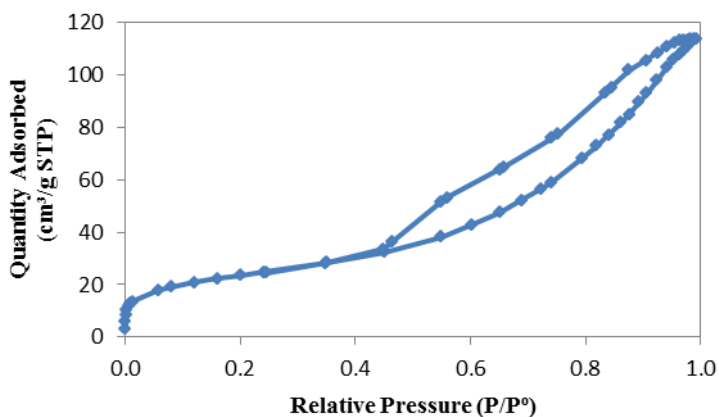
Deoxygenation of fatty acid leads to hydrocarbon production. After a non-catalytic thermal reaction, significant amount of alkane and alkene have been found in the liquid product from GC-MS analysis. It can tell that deoxygenation of fatty acid to alkane and alkene has occurred during the reaction. Therefore, it can be deduced that higher conversion of fatty acid lead to higher deoxygenation of the system. Due to complex mixture of different types of fatty acid present in the UPO, deoxygenation of major saturated fatty acid of UPO, which is palmitic acid was focus in the present study.

Catalyst characterization

The results of nitrogen adsorption surface analysis were summarized in Table 2. The catalyst was found to have large 60 Å pore size with 84.81 m²/g BET surface area. Nitrogen adsorption isotherm for the catalyst is shown in Figure 2. It is a type IV isotherm with hysteresis loop. The initial part of the Type IV isotherm was attributed to monolayer-multilayer adsorption [22].

Table 2. Physical properties of NiSnK/SiO₂ catalyst

Particular	Amount
BET surface area	84.81 m ² /g
t-plot micropore area	4.85 m ² /g
BJH Desorption average pore diameter	60 Å
BJH Desorption pore volume	0.18 cm ³ /g

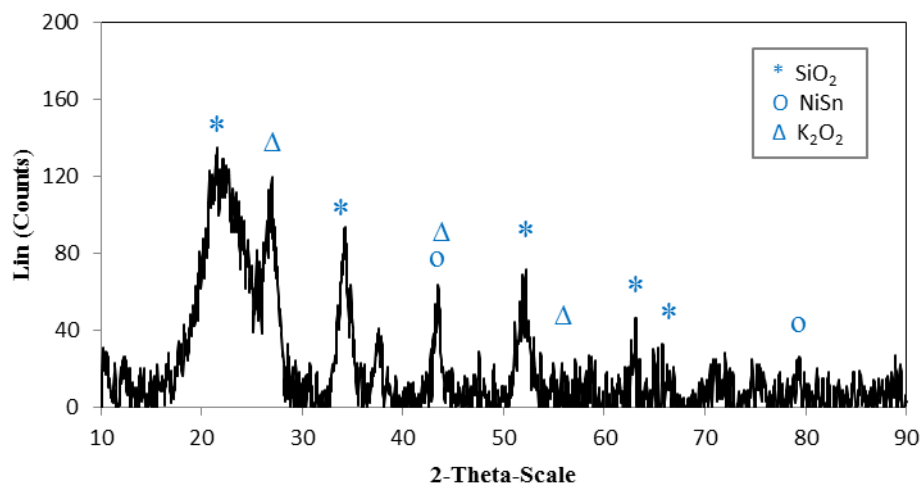
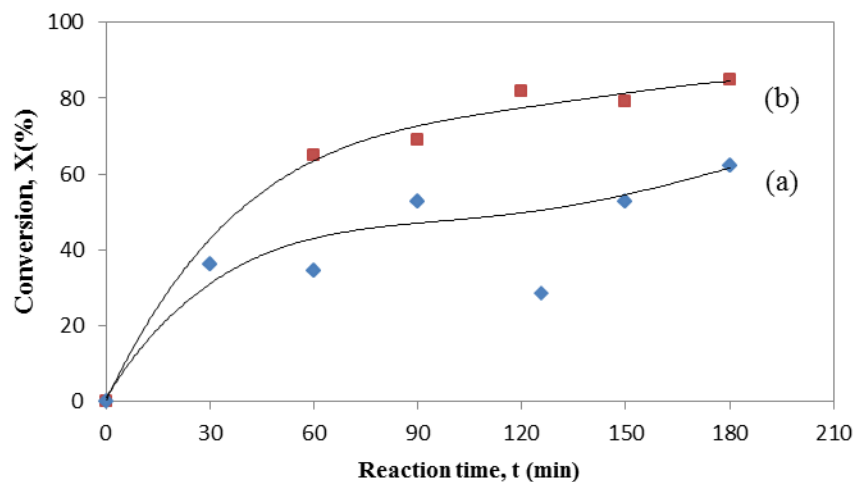
Figure 2. Nitrogen adsorption-desorption isotherm of NiSnK/SiO₂ catalyst

The XRD pattern of the catalyst is shown in Figure 3. Three different phases of the crystalline structure were identified, which were silicon oxide (SiO₂), nickel tin (NiSn) and potassium oxide (K₂O₂). Diffraction peak of silica used as support in the present study, appeared at 2θ of 22°, 34°, 52°, 63° and 65°. Diffraction peaks of nickel tin (NiSn) were observed at 2θ of 43° and 79°. Another phase identified was potassium oxide. The diffraction peaks of potassium oxide were observed at 2θ of 27°, 42° and 55°.

NiSn was observed and this could be due to both metal precursor of Ni and Sn were mixed and impregnated together during catalyst preparation. K₂O₂ was found because of oxidation of outer layer of potassium coating on NiSn/SiO₂ catalyst in the presence of air. Only potassium existed in oxide form. Potassium is more reactive than Ni and Sn, and hence more easily undergoes oxidation.

Deoxygenation of UPO

A catalytic deoxygenation reaction with NiSnK/SiO₂ as catalyst carried out at WHSV of 4 hr⁻¹ at 300°C was compared to a thermal reaction for the conversion of palmitic acid within UPO. The conversions of palmitic acid for both tests are showed in Figure 4. The conversions for both reactions seem to increase even after 3 hours of continuous reaction. This could be due to the system has yet reaching the steady state condition. Generally, reaction with catalyst had a higher conversion compared to that of without catalyst. The conversion of palmitic acid collected at 180 minutes for catalytic test was 84.96% compared to 62.13% in a non-catalytic test. The conversion has increased by 22.83% in the presence of catalyst, NiSnK/SiO₂. Therefore, deoxygenation reactions were further carried out for the effects of operating parameters.

Figure 3. X-ray diffraction pattern for NiSnK/SiO₂.Figure 4. Conversions of palmitic acid for (a) thermal and (b) catalytic deoxygenation (300°C, WHSV = 4 hr⁻¹).

Effect of WHSV on deoxygenation of UPO

In the present study, WHSV was varied by manipulating the flow rate of UPO while keeping the catalyst mass fix. The catalyst bed was kept in cylindrical shape at middle part of reactor with diameter of 0.8 cm and thickness of 1 cm. The size of catalyst bed was fixed in the present study in order to wipe out other factors that could have influenced the reaction rate such as mass transfer resistance and pressure drop. The effects of WHSV at 4, 6, and 8 hr⁻¹ on deoxygenation of UPO were studied and the results are presented in Figure 5. A linear decreasing trend in conversion of palmitic acid with WHSV was observed as expected. The trend obtained in this research was in agreement with Priecel et al. [23].

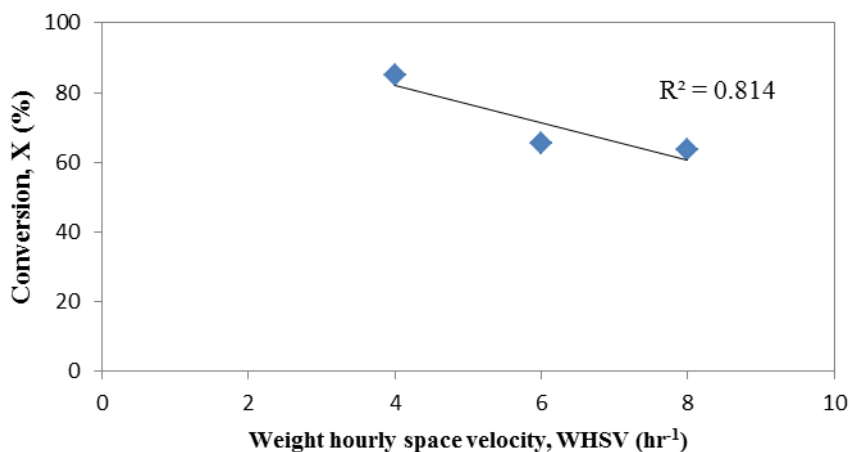


Figure 5. Effects of WHSV on the conversion of palmitic acid (sample collected at 180 mins, 300°C).

Effect of reaction temperature on deoxygenation of UPO

Three different reaction temperatures, 250°C, 300°C, and 350 °C were studied in deoxygenation of UPO using NiSnK/SiO₂ as the catalyst. WHSV of 4 hr⁻¹ was applied in this study since the highest conversion of palmitic acid was achieved with this WHSV. The effect of temperature on the conversion of palmitic acid is shown in Figure 6. A linear increasing trend of palmitic acid conversion with reaction temperature was observed. Similar trend had also been observed by other researchers [12, 18, 24, 25].

Higher conversion of palmitic acid achieved at higher temperature was expected as the deoxygenation reaction is endothermic and the reaction rate increase with the temperature. The conversion was the highest at 350°C proved that thermal stability of NiSnK/SiO₂ is reasonable. The catalyst able to withstand high temperature and maintains its catalytic activity at 350 °C.

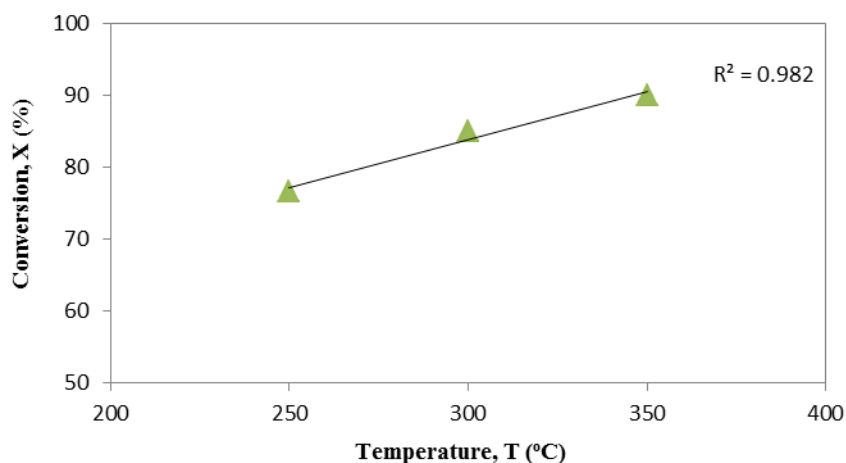
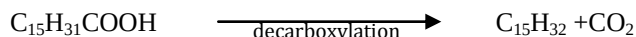


Figure 6. Effect of temperature on conversion of palmitic acid (sample collected at 180 mins, WHSV= 4 hr⁻¹).

Deoxygenation of palmitic acid

Palmitic acid was used as model compound of UPO in order to obtain further understanding on deoxygenation of UPO. WHSV was varied in order to observe products formed under different contact time. From the analysis, n-pentadecane product, C₁₅H₃₂ was detected in samples for all the reactions. N-pentadecane is an alkane with 15 carbon atoms, one carbon less than palmitic acid. Thus, it was produced via decarboxylation.



When the contact time for reaction was increased, additional three isomers of pentadecane were observed (2,5-dimethyltridecane, 4,8-dimethyltridecane and 2,7,10-trimethyldodecane). Besides that, pentadecene (C₁₅H₃₀) and its isomer, alkene with a double bond and one carbon less than palmitic acid was also observed. This was found to be the product of decarbonylation. Thus, the reaction mechanism for deoxygenation of palmitic acid is proposed, as shown in Figure 7.

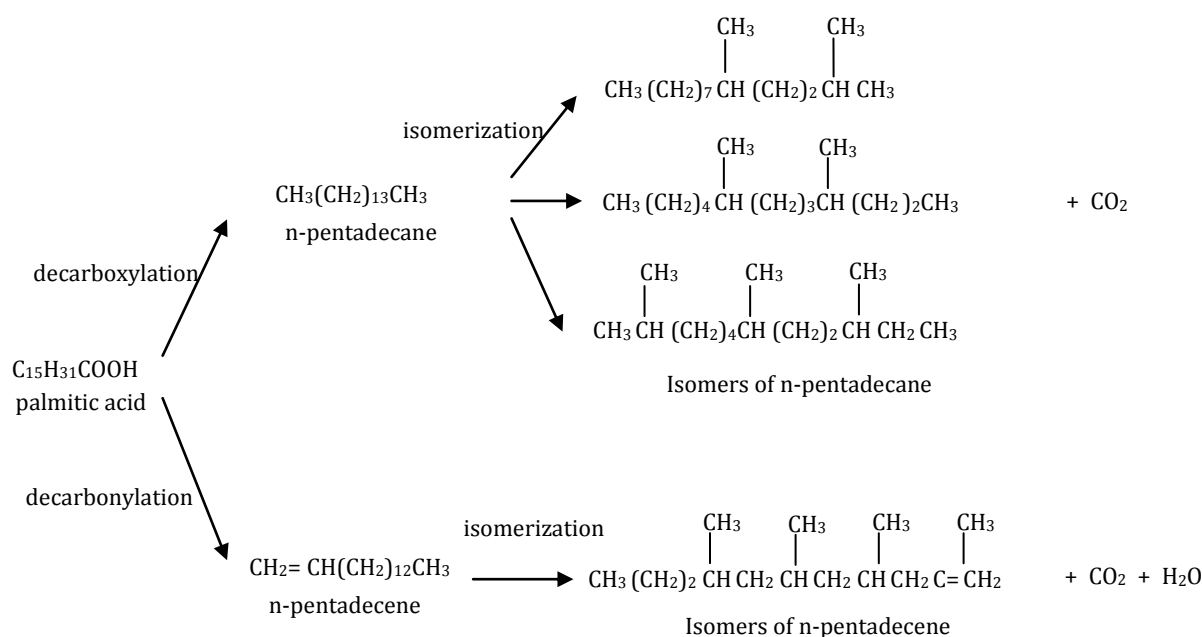


Figure 7. Reaction mechanism for deoxygenation of palmitic acid.

Conclusion

Deoxygenation of UPO with NiSnK/SiO₂ catalyst for the production of diesel-like hydrocarbon was investigated. NiSnK/SiO₂ was found to be an effective catalyst for the reactions. Conversion of palmitic acid, the major fatty acid in UPO was found to increase with reaction temperature and decrease with space velocity as expected. The highest conversion of palmitic acid in UPO, 90.08% was achieved in the present study at 350 °C. Reactions of palmitic acid model compound system proof that deoxygenation was via decarboxylation and decarbonylation.

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