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Catalytic Upgrading of Vegetable Oils into Jet Fuels Range Hydrocarbons Using Heterogeneous Catalysts: A Review

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Abstract

The production of high grade jet fuels from vegetable oils is an issue of special interest to refineries. The conversion process involved hydrotreating (i.e. hydrodeoxygenation and hydrodecarboxylation) of the oils followed by subsequent hydroisomerization. The paper reviewed recent literature on the role of heterogeneous catalysts in the various processes. Catalysts based on Ni and Mo supported on oxides are considered very active for the hydrotreating process whereas Pd and Pt supported on zeolites as the main hydroisomerization catalysts. However, further studies are still required on the role of catalyst topology, reaction mechanisms and the strategies for mitigating catalyst deactivation.

Keywords: vegetable oils; jet fuels; hydrotreatment; hydroisomerization; catalysis.

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1

1. Introduction

The production of vegetable oils is an important issue of global interest for decades before now. These oils are particularly attractive due to their renewable and environmental friendly nature and the possibility of conversion into energy fuels (i.e. fuels for energy generation). By the year 2000, the global productions of palm, soybean and rapeseed oils were 20, 25 and 15 million tonnes but increased to 50, 41 and 25 million tonnes in 2012, with further increase projected for the current and future years [1]. Vegetable oils are primarily employed in the energy industry for conversion into biodiesel, mostly via the process of catalytic transesterification [2], [3], [4], [5], [6] and [7]. However, the current trend in the global energy crisis as related to fossil fuels production and consumption accounted for evaluating the prospects of the vegetable oils in the production of jet fuels (i.e. biojet fuels) [8], [9], [10] and [11]. The jet fuels, otherwise referred to as aviation fuels, are mainly produced from the refining of petroleum feedstock for the purpose of powering aircrafts. They are suitable for use in both internal combustion and turbine engines (i.e. in both low and high temperature and pressure engines). The quality and specification requirements for these fuels such as the ability to burn without danger and cleanly, high calorific efficiency, chemical stability and low viscosity in compliance with low temperature implied that, the fuels can suitably be derived from renewable resources. Jet fuels are composed primarily of hydrocarbon compounds that include saturated straight and cyclic alkanes (could be up to 85%), aromatics especially benzene and low concentrations of olefins (usually 1%) [12], [13],[14] and [15]. Table 1 reports a typical composition of jet fuel sourced from either petroleum or shale [16] and [17].

The straight paraffin components are characterized by a high ratio of hydrogen to carbon and therefore give rise to high production of heat per unit mass compared to the other hydrocarbons. They are similarly capable of burning cleanly and are therefore required in large quantities in the aviation fuels. The cyclic paraffins are important for ensuring suitable density and reduced-freezing points of the fuels. The respective rapid smoke production and reactivity of aromatics and olefins during combustions accounted for their low concentration requirements. These compositions and features desired of high quality aviation fuels indicated that vegetable oils, which are mainly triglyceride esters, must undergo appropriate conversion processes. For this

2

reason, the biojet fuels are produced via catalytic hydrodeoxygenation (HDO)/hydrodecarboxylation (HDC) and catalytic isomerization (Scheme 1). Both HDO and HDC remove lighter hydrocarbon species like propane in addition to carbon dioxide and water. They proceed with the formation of even and odd-numbered chains of paraffins, respectively [18]. The isomerization process, on the other hand, converts the derived linear paraffins into corresponding isomers with enhanced biojet fuels properties. In all cases, the appropriate choice of reaction parameters such as catalyst, temperature, space velocity, feedstock and pressure is very critical in achieving optimal yields.

Please put Scheme 1 here.

Please insert Table 1 here.

1.1 Objectives of the Review

The paper presents a review on the role of heterogeneous catalyst systems for the conversion of vegetable oils into hydrocarbon compounds (i.e. paraffins) in the range suitable for jet fuels. Emphasis would be given to catalyst development and activity evaluation during conversion of the vegetable oils into n-paraffins through HDO/HDC and subsequent isomerization to high grade biojet fuels. To the best of our knowledge, no any critical review has been previously published on this specific subject. The paper will therefore provide a baseline for identifying the progress made and the ways forward. Heterogeneous catalysts are the main catalyst systems so far identified for this process due to their cost-effective nature and environmental sustainability in related reactions. Therefore, the paper will mainly focus on these catalytic materials. Noble metals (i.e. platinum group metals like Pt, Pd, Ru etc.) and composite transition metal catalysts based on NiMo, CoMo, NiCo and their supported analogues were reportedly studied for the HDO/HDC reactions whereas zeolitic materials as the candidates for isomerization due to their structure-acidity properties. The paper covers concise details on these materials, with emphasis to their activities and operation conditions. Factors responsible for catalyst deactivation and the

3

regeneration methods would also be discussed. Homogeneous catalyst systems have not been captured because they are not being employed for this process due to their associated recyclability, disposal/environmental, corrosion and costly problems.

2. Hydrodeoxygenation (HDO) and Hydrodecarboxylation (HDC) of Vegetable Oils

Both hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) are simultaneous hydrotreatment processes that occur during the upgrading of petroleum feedstock, but the scope have recently be extended to include the upgrading of biomass-based feedstock like the vegetable oils. The HDO proceeds by the removal of oxygen from oxygenated compounds (i.e. oxygen containing compounds) in the feed following the incorporation of hydrogen and an appropriate catalyst. With vegetable oils, the long chain glyceride esters contain carbonyl oxygens that could be removed via the HDO reaction. On the other hand, the HDC reaction involved the removal of carboxyl groups in both fatty acids and esters of the vegetable oils, usually with the emission of CO_2 gas during the reaction. The catalytic production of liquid alkanes (i.e. linear and branched) from vegetable oils by the HDO and HDC reactions offers an important alternative for handling numerous disadvantages including stability and miscibility problems. However, the most appropriate catalysts are still being investigated according to the present literature [18]. Noble metals (i.e. the platinum group metals such as Pd, Pt, Ru etc. known for their resistance to oxidation or corrosion in moist air) are usually supported with zeolites or oxides and employed as catalysts for the HDO/HDC reactions. They were the early materials studied with a later shift to other transition metals like Ni, Mo, Co, Mo or their supported bimetallic composites [19]. The HDO and HDC of vegetable oils, which normally occur simultaneously, were first commercialized by the Finland Company, Neste Oil [20] and [21]. The goal of the company was to develop gasoline, biodiesel and jet fuels from renewable feedstock without any compromise to fuel properties, engines specifications or international emission standards [22] and [23]. Ability of vegetable oils to be hydrotreated into valuable paraffinic fuels without sulfur or aromatic compounds is the promising factor relied by the company. The Neste Technology operates on the basis of existing refinery mechanism (see Figure 1). Vegetable oils can be mixed with fossil feeds and fed into the existing process units [21]. Following this development, several other production units are being developed around the

4

globe by oil companies [20, 21]. In fact, the market for these types of fuels have been predicted to rise from 6% in 2010 to about 12% in 2018 with further increase for the subsequent years [22] and [24]. Therefore research, especially with emphasis to catalyst development and operation parameters, needs a speedy intensification. The identification of most suitable catalysts in terms of vegetable oil conversion, selectivity to jet fuels range paraffins and stability properties would elevate the economic viability and sustainability of the overall process. Evaluation of heterogeneous catalysts would therefore be very important due to their numerous advantages. They can easily and cheaply be recovered after the reaction. They are characterized by good thermal stability and enhanced selectivity to desired reaction products. The exploitation of homogeneous catalysts could be associated with challenges such as poor thermal stability, difficult and expensive recovery nature and environmental disposal problems.

Please insert Figure 1 here.

2.1 Reactions with Noble Metals

Among the noble metals known today, Pd, Ru and Pt are the main industrial materials evaluated for the HDO and HDC reactions. Wildscht et al. [25] employed 5 wt.% of Ru, Pt and Pd each supported over Al_2O_3, C or TiO_2 for HDO of oil at variable temperatures and pressures and 0.11 h^{-1} space velocity for 4 h. Under these conditions, the Ru/C catalyst formed the best HDO catalyst with 90% yield of desired products (i.e. liquid alkanes, C_5 to C_{16}). Reactions over Pt or Pd produced large quantities of CO_2 and associated gases (up to 60%), irrespective of the support nature, especially at elevated temperatures reaching 350^oC. The possibility of side reactions such as cracking, polymerization and hydrogenolysis with potentials for carbonaceous depositions dominated the reactions over the latter materials. Catalysts supported with Al_2O_3 exhibited poor performance due to low surface area and stability challenges. Similarly, the active acidic sites of Al_2O_3 were susceptible to poisoning by water in addition to crystallite rupture. However, a study by Madsen et al. [26] which employed similar loading of Pt or Pd (i.e. 5 wt.%) over Al_2O_3 reported high degree of HDO and HDC with Pt supported catalyst at 325^oC and 20 bar of

5

hydrogen pressure. Oil conversion and products yield reached ~100%. The higher ratio of odd to even number chains of paraffins indicated the HDC activity to supersede the HDO activity of this catalyst. Interference by fatty acid formation/participation was found to have a negative effect on products yield, especially with supported Pd catalyst. The coversion and yield of n-C_5 to n-C_{15} reduced to 46 and 6%, respectively. Murata et al. [27] conducted the processing of jatropha oil with Pt-Re catalyst supported over H-ZSM-5 zeolite at 300°C and oil to catalyst ratio of 1. Their characterization data showed both Pt and Re to exist as separate active species over the support, although with possibility of synergic interaction. The reaction products were mainly n-C_{15} to n-C_{18} alkanes, with the concentration being much dependent on the ratio of oil to catalyst. At the initial ratio of 1, the n-alkanes yield reaches 80% but decayed to only 2.3% when the ratio was further raised to 10. However, the synergic effect slightly retards the decay process. Similarly, the reaction mechanism over these metal sites was consistent with Scheme 1. The C=C bonds in the triglycerides were first hydrogenated and both the HDO and HDC reactions occurred simultaneously. Although the values of the BET surface areas of the catalysts were almost similar, production of cracking species was severe with either Pt/H-ZSM-5 or Re/H-ZSM-5 than the synergic Pt-Re/H-ZSM-5 catalyst. The yields to cracking products for the Pt/H-ZSM-5, Re/H-ZSM-5 and Pt-Re/H-ZSM-5 were 60, 20 and < 5%, respectively. A study on the actual reaction pathways and effect of Pd, Pt and Ru supported with Al_2O_3 (of variable loadings, 39.7 to 91.9%) for the hydrotreating of soybean oil was recently performed by Veriansyah et al. [28]. The reactions were carried out at 400°C and 92 bar hydrogen pressure for a period of 2 h. The reaction pathways were also generally consistent with the illustrations in Scheme 1. Paraffin products from the reaction were mainly n-C_8 to n-C_{18} species, with negligible amount of n-C_{19} and n-C_{20} (< 1%). Hydrodecarboxylation proceeds with the production of n-alkanes with odd number of carbon atoms (n-C_{15}, n-C_{17} etc.). Interestingly, n-alkane species were also generated through the successful reaction of free fatty acids in the soybean oil feed with hydrogen. In a similar trend, the HDO reactions yielded products with an even number of carbon chains (n-C_{16}, n-C_{18} etc.). On the other hand, low molecular weight species such as CO and CO_2 produced interacted with the hydrogen via methanation, producing methane gas and in some instances by water-gas shift process (Scheme 2). The overall reaction trend is also in good agreement with the work of other authors like Huber et al. [29]. Catalytic activity of the noble metals followed the order Pd>Pt>Ru. The Pd catalyst produced the highest concentration of n-alkanes (86%)

6

followed by Pt (41%) and Ru yielded the least concentration of 39%. Similarly, the soybean oil conversions were 92, 51 and 40% for Pd, Pt and Ru catalysts, respectively. Low activity of Ru under these conditions was attributed to carbonaceous depositions due to cracking reactions as also reported previously [30] and [31]. Species such as cyclic and isomerized alkanes and aromatics, that are associated with good flow properties at low temperature, were not detected with all the materials, suggesting the HDO and HDC as the main reaction pathways.

Please insert Scheme 2 here.

Mohammed et al. [32] and other workers [33],[34] and [35] have reported a number of reasons for the poor performance of these materials during the hydrotreatment reactions. Depending on the nature of the support, enhanced reaction temperatures favor catalytic cracking associated with catalyst acidity. For example, According to Duan et al [36], an acidic 5 wt.% Pd/Al-SBA-15 catalyst produced almost 100% sunflower oil conversion with 73% yield of C_{15} to C_{18} alkanes at $250^{o}C$. However, when the temperature was raised to $300^{o}C$ the yield dropped to ~53% due to C-C bond breakage associated with combined effect of high temperature and catalyst acidity. HDC may dominate the HDO reaction thereby increasing the ratio of odd/even number of carbon chains. This contributes greatly to product fission and the formation of lighter unwanted species (i.e. C_1 to C_4 hydrocarbons). Noble metals are susceptible to sintering at elevated temperatures and could therefore experience activity decay with time. Chu and Ruckenstein [37] showed Pd particles supported over alumina to sinter at $500^{o}C$ in H_2 atmosphere. The crystallite particles of 5.5 nm size sintered to 9 nm after 6 h and later to 16.2 nm when the temperature was raised to $650^{o}C$ for 3 h. HDO reaction proceeds with the elimination of water molecules (see Scheme 1) that can poison the active noble metal sites. In addition to all these inconsistencies, the noble metals were proven to be expensive, making the overall process unviable. Therefore, accounting for a shift to alternative materials. Catalyst deactivation may also be encountered depending on the feedstock or reaction parameters. For example, the work of Madsen and co-workers [38] showed the activity of a 2 wt.%Pd/Sibunit to depend on these factors at $300^{o}C$. When the reaction was carried out with 5% H_2 in Ar as sweeping gas, excellent yields of hydrocarbons with potentials for jet fuels were obtained but the catalyst deactivation properties depend on the

7

feedstock nature. The respective initial yields for stearic acid, ethyl stearate and tristearin were >90, >90 and 85%, but these values reduced to 75, 62 and 25%, respectively after 75 h of reaction. The worst scenario was observed when the reaction was performed in 100% Ar atmosphere. In this case, the respective yields dropped to 3, 0 and 0% due to complete catalyst deactivation. The catalyst deactivation was attributed to coke deposition and the presence of impurities like fatty acids and metals.

2.2 Reactions with Other Transition Metals

For the purpose of this paper, other transition metals refer to pure Ni, Mo, Co, W, their composites (i.e. bimetallic or trimetallic systems) or even the supported materials. These materials, especially the sulfide compounds, have been previously tested in the hydrotreatment of petroleum fractions [39],[40],[41],[42] and [43], and are therefore currently being evaluated as replacement catalysts for the HDO and HDC of vegetable oils.

2.2.1 Effect of Catalyst Support

The catalyst support represents an important material employed during heterogeneous reactions to enhance the activity of the overall active components of the catalyst, by increasing dispersion and accessibility by reacting species. Supports which could be oxides, carbon, zeolites, heteropoly acids etc, are normally solid materials of the large active surface area for deposition of active catalyst components. They play vital roles in reactions where participation of surface catalyst sites is necessary. Supports could either be neutral or containing active sites that also participate in the reaction forming bifunctional (i.e. dual function) catalysts. Therefore, the neutrality, acidity or basicity of a support must carefully be considered before employing it for catalyst design. Historically, transition metals (i.e. pure Ni, Mo, Co, W and their composites) for HDO/HDC reaction can be supported on oxides, zeolites or carbon. However, supports with moderate acidity are always preferred because high acidity causes cracking of the generated n-alkanes and therefore reduces their selectivity. For example, studies by Centeno and co-workers demonstrated the nature of the support to influence HDO/HDC activity of supported CoMoS catalyst. Moderately acidic supports were good candidates for carboxyl groups HDO [44]. They reported 80% conversion of pyrolysis oil with CoMoS supported on carbon and 60% when alumina was employed as the support. However, activity of supports like alumina can be promoted by its Lewis acidity. A model study by Ryymin et al [45] conducted at $250^{\circ}C$ and 75

8

bar using sulfided $NiMo/Al_2O_3$ catalyst produced 100% conversion of methylheptanoate in 3 h. n-heptane was the dominant reaction product (~ 90% selectivity). Similarly, no sulphur containing products were detected. Wang et al. [46] examined the role of a range of zeolite supports on the activity of Ni catalysts. Reactions were conducted at 370^oC with a space velocity of $1.0 h^{-1}$ and 40 bar pressure. Ni particles were successfully doped over all the zeolite supports via impregnation method, as indicated by the various characterization data. The soybean oil feed was rich in both saturated and unsaturated triglycerides of C_{16} and C_{18}, respectively. Although, the soybean oil conversion over all the materials was nearly 100%, catalysts with moderate acidity were more selective to the formation of liquid alkanes (i.e. both n- and i-) with limited cracking. Ni/ZSM-5 being the most acidic showed 52% cracking with difficult to detect amount of desired liquid hydrocarbon products when compared to Ni/H-ZSM-22 and Ni/H-ZSM-23 that produced 50 and 53% of liquid hydrocarbon products, respectively. The best SAPO-11 support of moderate acidity showed the highest selectivity (i.e. 100% selective to $n-C_7-C_{14}$ alkanes), that was also dependent on the Ni loading. Over this material, increasing the Ni loading from 0 to 8 wt% reduces the amounts of strong acid sites and permits the availability of active Ni sites. A consequence was the production of isomerized alkanes by 85%. Some authors [47],[48] and [49] have demonstrated isomerization of activity of n-alkanes to be favored by moderated acidity and presence of effective metal sites. The reaction was also found to be temperature and space velocity dependent. For example, with the 8 wt%Ni/SAPO-11, raising the temperature from 300 to 340^oC increased soy bean oil conversion from 75 to 100% whereas C_7 to C_{14} alkanes from 63 to 99%. The selectivity to isomerized alkanes also increased from 20 to 46% [46]. On the other hand, the conversion dropped from 100 to 23% when the space velocity was raised from 1 to 30 h^{-1}. Under this condition, selectivity to alkanes decreased from 100 to only 16% whereas isomerization from 87 to only 5% [46]. The various studies indicated moderate acidity of the support as a positive parameter for achieving high yield of liquid alkanes. However, the reaction must be carried out at moderate to low reaction temperatures. At high temperatures, hydrocracking with production of ligher gaseous hydrocarbons (i.e. C_1 to C_4 compounds) could dominate the reaction. Approriate loadings of active metal (s) are also very critical for this reaction.

9

2.2.2 Effect of Catalyst Composition and Reaction Conditions

The nature of the various catalyst components (i.e. active sites, support, etc) can influence its catalytic activity and selectivity properties. Similarly, the reaction parameters such as temperature, feed composition, pressure, catalyst preparation method and space velocity. The upgrading activities of Pt supported over zeolites H-ZSM-5 and H-Y and NiMo supported with Al_2O_3 was studied by Sotelo-Boyas and co-workers [50]. The NiMo catalyst was prepared from crushing and sulfidation of the precursor oxides whereas 2wt.% of Pt was introduced into each zeolite support via impregnation. Reactions were carried out at temperatures of 300 to 400°C and 5 to 110 bar pressure, employing 3 wt.% of catalyst to rapeseed oil for a 3 h period. The initial high consumption of hydrogen during the reaction was attributed to the high degree of unsaturation associated with triglycerides and free acids in the rapeseed oil. Over all the catalysts, the conversion was amost 100% and the reaction mechanism was the same, involving HDO and HDC. Similarly, increasing the reaction temperature lowers the yield of desired n-alkanes, with the effect being more severe for the Pt/H-Y and Pt/H-ZSM-5 catalysts. At high reaction temperatures, the n-alkanes underwent cracking reaction producing lighter (i.e. C_1 to C_4) hydrocarbons. Reactions over NiMo/Al_2O_3 catalyst produced the highest amount (up to 90%) of n-C_{15} to n-C_{18} irrespective of the reaction conditions. Pt/H-ZSM-5 yields the highest amount of C_1 to C_4 cracking species of 21% due to stronger acid sites than Pt/H-Y which produced less than 4%, consistent with other studies [51],[52] and [53]. On the other hand, the initial hydrogen consumption could be limited by appropriate sulfidation of the NiMo. This factor can have positive effect on the net catalytic selectivity towards the desired n-alkanes [54]. Another interesting fact is that, catalytic activity of the transition metals can also be influenced by nature of modification and structure. Recently, Zhang et al. [55] modified MoS_2 with Ni and Co and evaluated the activity of the resulting catalyst systems during upgrading of canola oil. The reactions were carried out at 375°C, 85 bar hydrogen pressure and 1/200 catalyst to oil ratio for a period of 8 h. Catalysts were characterized by TEM and TPR to exist as NiMoS and CoMoS of highly dispersed nano-particles. Catalytic activity was found to be structure dependent, because Ni and Co can differ in their mode of interaction with MoS_2 [56], [57], [58]. NiMoS was more active to HDO whereas CoMoS produced most of the reaction products through HDC or even

10

hydrodecarbonylation. Although both catalysts produced closer conversion of almost 100%, formation of hydrogenolysis species was more severe with the CoMoS material. On the other hand, the synergic association between Ni and Co particles promoted the production of n-C_7 to n-C_{18} alkanes to > 90% selectivity via the HDO mechanism. Kubicka and Horacek [59] indicated the presence of prospective catalyst poisons such as water, fatty acids and lipid-based impurities to affect the activity of CoMoS supported with alumina during rapeseed oil hydrotreating at 310^oC and a hydrogen pressure of 35 bar. Without the impurities, the reaction was very fast, producing mainly higher desired alkanes (n-C_7 to n-C_{17}). However, the impurities posed the reaction to proceeds slowly with lost after some time. The refined rapeseed oil without any impurities produced almost 100% conversion that reduced only to 96% after 100 h. However, an impure/waste rapeseed oil showed a gradual conversion decay from 100 to 75% for the same period. Impurities attack the active catalyst sites and halt the reaction by poisoning. In some instances, the reaction can be more selective to the formation of much lighter undesired species [60], [61] and [62]. The role of sulfur is to promote catalyst stability and ensure the availability of active metal sites for the reaction [45]. However, presence of hydrogen in the reaction feed may also have a negative effect because it can react with sulfur at high temperatures to produce H_2S and lower the catalytic activity.

A study on thermal and pressure effect was recently reported by some authors [63], who employed NiMo catalyst for upgrading olive and corn oils at 320^oC and 1.0 h^{-1}. Catalytic activity depends on the nature of the feedstock and the reaction pressure. Approximately, 71 and 32% yields of n-alkanes (n-C_7 to n-C_{18}) were observed with 20% olive oil at 3.0 and 60 bar, respectively. On the other hand, the respective values were 67 and 29% for the corn oil. The thermal effect was relatively the same irrespective of the hydrogen pressure. However, the degree of unsaturation associated with fatty acids in the oil feeds influences the thermal effect positively. Interestingly, NiMo catalyst shows a limited cracking, producing mainly C_1 to C_5 species in trace quantities as expected [64]. No subsequent activity decay was observed under these conditions. However, lighter products from methanation and water-gas reactions were produced consistent with Scheme 2.

The synergic role of the incorporation of an additional metal was also demonstrated by Kubicka and Kaluza [65]. They employed Ni, Mo and NiMo supported with alumina for upgrading a

11

food-grade rapeseed oil at variable temperatures (300°C <), space velocities (0.25 to 4.0 h^{-1}) and 35 bar pressure. Under all the reaction conditions, supported NiMo catalyst produced the best activity attributed to synergic metallic interactions. For example at 270°C and 1 h^{-1}, the NiMo catalyst produced almost 100% conversion compared 80% obtained with each of the Mo and Ni catalysts. While the selectivity of C_5 to C_{15} alkanes was nearly 100% with NiMo systems, the Ni and Mo catalysts produced respective selectivities of 60 and 50% under these conditions. Reactions over the Ni/Al_2O_3 involved both HDO and HDC but with the formation of undesired oxygenated intermediates. The Mo/Al_2O_3 on the other hand, produced low yields of alkanes via only the HDO route. The synergic effect favor the formation of desired fuel-grade alkanes [66] and [67]. Liu et al. [68] showed modification of the alumina support with silica to further enhanced the hydrotreatment activity of the NiMo catalysts. The $NiMo/SiO_2-Al_2O_3$ catalyst produced ~100% conversion with > 90% selectivity compared to ~90% and < 80% observed with the other catalysts containing only silica or alumina support. It was also resistance to deactivation by 15% fatty acids in the original jatropha oil feedstock. Interestingly, a study by Harnos et al. [35] revealed the synergic effect of NiMo supported over alumina to be effective even without sulfidation. The authors evaluated the activity of a range of Ni loadings and NiMo material supported with alumina for upgrading sunflower oil at a pressure of 21 bar and temperature of 340°C (with or without sulfidation). Irrespective of the Ni loading, sulfidation was necessary to promote catalyst stability contrary to what was observed with supported NiMo catalyst. Ni/Al_2O_3 materials were more active to side reactions, producing lighter undesired products. Both HDO and HDC mechanisms were observed with these catalysts but the formation of n-C_{17} and n-C_{18} alkanes predominated the NiMo catalyst even without sulfidation. According to Kimura et al. [69], the excellent activity can be achieved even at low hydrogen pressure. The authors upgraded coconut oil with unsulfided $NiMo/Al_2O_3$ catalyst at hydrogen pressure below 10 bar, 5,000 h^{-1} and 350°C. Oil conversion reaches 97% and the yields of jet fuel grade alkanes with carbon number in the range of C_5 to C_{17} was 94%. They attributed the low hydrogen pressure to promote the formation of intermediate species with good alkanes' generation potentials. Recently, Horacek et al.[70] investigated the effect of W addition in comparison to Co or Ni with Mo during rapeseed oil upgrading at 250°C and variable contact times. The resulting activity follows the order NiMo>CoMo>WMo. At 250°C and 1 h^{-1}, the respective conversions for the NiMo, CoMo and WMo catalysts were 100, 80 and 60%. Similarly, the corresponding

12

selectivity to liquid alkanes were 98, 70 and 50%, respectively. Synergic interaction between Ni and Mo was more pronounced than with other metals, and consequently favoring the catalytic performance. However, the co-presence of both Ni and Co (i.e. to form NiCoMo catalyst) caused a double increase in HDO activity than the least active material. The authors also found the synergism to be support dependent. Catalysts supported over SiO_2 were more active producing 80 to almost 100% conversion than those supported over Al_2O_3 or TiO_2 that produced < 80% conversions under comparable reaction conditions. As expected, HDC reactions dominated the latter materials [71]. On the other hand, SBA-15 supported catalysts were preferred for the HDO reactions, especially when promoted with silica to form SiO_2-SBA-15 support. Trimetallic systems demonstrated improved performance in all cases. The reaction products composed mainly of alkanes (both n- and i-) to > 85% selectivity with limited side reactions. These types of catalysts should further be evaluated to fully establish their modes of action, the extent of inter-metallic synergic interaction and how the addition of a third metal modifies the catalyst textural surface.

2.2.3 Role of Catalyst Modification with Metal or Phosphorus

Supported catalysts based on NiMo have so far demonstrated promising activity and selectivity properties during the HDO/HDC upgrading of vegetable oils. However, problems of poor catalyst lifetime (i.e. catalyst deactivation with time) are common. The incorporation of appropriate modifier (e.g. metal, phosphorous, etc) can enhance the stability properties. Modification of supported NiMo catalysts with boron and/or phosphorous had been reported to have positive effect on the support acidity and consequently the hydrotreatment activities [72],[73]. Ferdous et al [72] modified a NiMo/Al_2O_3 catalyst with 1.7 wt.% boron and 2.7 wt.% phosphorous by treatment with boric and phosphoric acids, respectively. Although the activity of the parent/unmodified NiMo catalyst was very high (> 95% conversion), it shows deactivation with time. However, modification with either boron or phosphorous ensures activity stabilization through the generation of new active acid sites and inhibition of coke deposition. For example, without modification, the hydrotreatment conversion of NiMo/Al_2O_3 at 450°C was 96% and quickly decayed with time but remained stable at 97% for almost 30 days following the modification. The trend was also constant even when the reaction temperature was raised to 500°C. This stability trend is similar to that reported by some other authors [73],[74]. Yang et al.

13

[75] have also showed a combined modification with phosphorous and MgO support to further promote both catalyst stability and acidity properties. Without these species, the conversion was around 64% but increased to >97% after the modification with a closely similar effect on products selectivity. Wang et al. [76] demonstrated La or Co addition to the boron modified NiMo catalyst to favor catalytic performance during HDO of phenol as a model compound. Catalytic studies were carried out employing a hydrogen pressure of 40 bar, 0.05 g of catalyst and 11.70 g of phenol for a period of 10 h. Boron addition modifies catalyst acidity through the creation of new active acid sites, La and Co ensured the stabilization of the active BET surface area of the parent catalyst and also favors metallic synergism. Both boron and lanthanum or cobalt modified catalysts produced nearly 100% conversion with product selectivity reaching 90%. The catalysts were stable for 10 h with negligible coke deposition. Therefore, although catalyst regeneration strategies are available for restoring the activity of coked catalyst, preventing the deactivation in situ will be more economical for the industry. The enhanced activity and stability properties demonstrated by the metals and phosphorous modifiers present an alternative for improving the prospects of the overall process. However, further studies are still essential to fully establish the most appropriate modifier loading suitable for commercial applications and the applicable reaction conditions.

2.2.4 Recent HDO and HDC Studies with other Transition Metals

A summary of some recent studies on the behaviors of the transition metals-based catalysts during the hydroprocessing of some vegetable oils under variable conditions has also been presented in Table 2 [77],[78],[79],[80],[81],[82],[83],[84]. In all the cases, the reactions proceed via the HDO/HDC mechanism, with the side reactions being mainly of methanation and water-gas types. The main reaction products were n- and i-alkanes with carbon chains in the range of C_7 to C_{18} (i.e. potentials for biojet fuels). Among these, the higher alkanes (i.e. C_{16} to C_{18}) could be successfully cracked to lighter liquid alkanes with 15 or less-carbon numbers over hydrocracking catalysts like the acidic zeolites prior to hydroisomerization . It could be established that, catalytic activity was dependent on several factors that include the nature of the catalyst, operation conditions, nature of the support, metal loading and in some instances the incorporation of a second or third metal. According to Srifa and co-workers [77], increasing the the hydrogen/oil ratio from 1000 to 2000 led to the formation of mainly liquid alkanes (i.e.

14

selectivity increased from 0 to 100%). At the lower ratio of 1000, only solid alkanes were produced (28%). These compounds can however be converted into the C_5 to C_{15} alkanes by hydrocracking with zeolite catalysts. NiMo catalysts supported with Al_2O_3 have generally demonstrated good activity toward alkanes' production, with limited degree of side reactions than supported CoMo catalysts. Modification of Al_2O_3 with B_2O_3 may have a negative effect on the alkanes yield. Similarly, SiO_2 being less acidic was more favorable to production of alkanes than H-Y for the Ni_2P catalyst under constant conditions. According to Zarchin et al [78], with 25 wt.% Ni_2P/SiO_2, the soybean oil yields 84% of desired alkanes compared to 78% obtained with 25 wt.% Ni_2P/H-Y catalyst. Promotion of Ni with Mo or W produces a comparable activity under constant conditions. Modification of $NiMo/Al_2O_3$ system with 1 to 25 wt.% of Ce showed slight modification to the hydrotreating properties of jatropha oil. At both low and high loadings (i.e. 1 to 25 wt.%), the selectivity to alkanes was in the range of 89 to 91% [83]. Lowering the reaction temperature from 320 to 280°C had a positive effect on the production of alkanes from palm oil using 7 wt.%Ni/SAPO-11 catalyst. It could be seen that, the selectivity increased from 44 to 79% when the temperature was reduced from 320 to 280°C [84]. A similar trend could be observed by increasing the loading of Ni particles. When the loading was increased from 2 to 7 and 9 wt.%, the selectivity to alkanes increased from 60 to 67 and 68%, respectively [80].

Please insert Table 2 here.

2.3 Catalyst Deactivation during HDO/HDC of Vegetable Oils

Catalyst deactivation involved the decay of catalytic performance (i.e. activity) or the associated reduction in selectivity to desired reaction products over time. The mode of the deactivation process is usually dependent on the reaction being carried out. Catalyst replacement usually posed a great challenge to refineries due to the costs involved. Therefore, understanding the processes of catalyst deactivation and the appropriate strategies for mitigating the catalyst deactivation would be very beneficial for the industry. Several catalysts deactivation routes are known. These include fouling (i.e. the deposition of materials like coke that cover the catalyst active sites), poisoning by the interaction of catalyst with poisons such as gases, water, metals,

15

etc in the reaction stream or produced during the reaction, catalyst decomposition by heat (i.e. thermal degradation) and agglomeration of the active catalyst particles by sintering process (i.e. crystallite growth).

Catalyst deactivation during HDO/HDC of vegetable oils depend on the nature of the catalyst and the compositions of the vegetable oil feedstock. Noble metal catalysts are associated with low thermal stability and could therefore be sintered at elevated temperatures. At reaction temperatures reaching $500^{\circ}C$, active Pd or Pt particles could be sintered by agglomeration (i.e. crystallite growth) [37]. This reduces accessibility be reactants due to the reduction in the active catalyst surface area with a consequent reduction in the yields of hydrocarbon products (particularly the C_5 to C_{15} alkanes required for jet fuels). The hydrodeoxygenation (HDO), in particular, produces water molecules that can destroy active noble metal catalyst sites by poisoning due to high sensitivity to poisons of these catalysts [38]. Catalyst containing sulphur such as CoMoS are more susceptible to deactivation by impurities like fatty acids and lipid-based impurities or water in the vegetable oil feeds [59]. These impurities strongly interact with active CoMoS catalyst sites and caused poisoning with a great negative consequence of lowering catalytic activity. Therefore, reaction with refined vegetable oils would be a very good alternative. Another problem with sulphur-containing catalysts is the removal of the sulphur species at high temperature via hydrogenation (i.e. interaction of catalyst with hydrogen employed for the reaction). The H_2S produced under this condition can also serve as a catalyst poison. The poisoning normally occurs through the strong interaction of these impurities. This trigger active sites blockage, destroy geometric catalyst structure and consequently cause activity loss. The reaction selectivity is usually shifted towards the formation of lighter undesired C_1 to C_4 hydrocarbons [60], [61] and [62].

Deposition of carbonaceous residues (i.e. coke formation) had been observed with some Ni containing catalysts (e.g. Ni and NiCo catalysts) or noble metals supported zeolites during the HDO/HDC reaction. The carbonaceous materials could be produced from polyaromatics or very long chain aliphatic hydrocarbons generated during the reaction. With zeolites, the pores are consequently blocked and this hinders the diffusion of both reactants and reaction products [46]. On the other hand, with Ni supported oxide catalysts, the active nickel sites are usually covered with a net destruction effect [64] and [70].

16

The deactivated HDO/HDC catalyst could be regenerated depending on the deactivation mode. The regeneration process restores the catalyst active sites, mitigating the need for fresh catalyst incorporation and therefore reduces process cost. Deactivation by sintering (usually for the Pd and Pt catalysts) has shown regeneration difficulties due to the complete agglomeration of the active catalyst particles [37] and [38]. However, HDO/HDC catalysts such as the Ni-based catalysts deactivated by carbonaceous deposits are more prone to regeneration, producing comparable activity to the fresh catalyst. This could be achieved by exposing the coked catalyst (i.e. catalyst deactivated by carbonaceous deposits) to hot air, which burns the deposits from the catalyst surface [56], [57] and [58]. However, high coke-oxidation temperatures like $700^{o}C$ must be avoided to prevent catalyst sintering. Prior to further cycles of HDO/HDC reaction, the regenerated catalyst could be reduced in hydrogen or carefully acidified to ensure full restoring of the active sites.

3. Hydroisomerization of the HDO and HDC Products

The normal paraffinic hydrocarbons produced from the HDO and HDC of vegetable oils are associated with non-compatible cold flow characteristics. They can therefore only be blended in low ratios with jet fuels. To appropriately improve these properties, the n-paraffins must be converted/upgraded into the corresponding iso-paraffins by the process of hydroisomerization (see Fig. 2) [85],[86] and [87]. However, when the chain length of the n-alkane produced from the HDO/HDC reaction exceeds n-C_{15}, a further hydrocracking to lighter alkanes in the range of n-C_5 to n-C_{15} is necessary before the hydroisomerization reaction [85]. The hydrocracking of alkanes is a known industrial process already developed by the petroleum refineries for the production of gaseous hydrocarbons, gasoline, kerosene etc. from heavy fractions [88-90]. An interesting issue here is that, the alkanes-hydrocracking can simultaneously be carried out with the hydroisomerization process using acidic zeolite catalysts [91-93]. However, very high temperatures (eg. $> 600^{o}C$) must be avoided as these can lead to the production of mainly C_1 to C_4 cracking hydrocarbons [94, 95].

Please insert Figure 2 here.

17

Hydroisomerization is an industrial process employed by petroleum refineries for the transformation of linear paraffins into their corresponding isomers at usually high hydrogen pressure (at least 20 bars), although recent studies indicated that the reaction can be achieved at 1 atm. The technology remains the main environmentally sustainable option for upgrading gasoline pool since the phased-out of toxic additives like tetraethyl lead (TEL) and methyl cyclopentadienyl manganese tricarbonyl (MCT) in the early 1990's. Therefore extension towards paraffinic jet fuels upgrading is a latest development. The process normally proceeds over a supported catalyst with bifunctionality (i.e. containing both the metal and acid sites) [96],[97],[98],[99],[100],[101] and [102]. Normal paraffin to be converted undergo initial dehydrogenation over the metal sites to produce a corresponding n-alkene with the same number of carbon chains. The interaction of the latter with Brønsted acid sites generates carbenium ion, which undergo subsequent isomerization into iso-carbenium ion and consequently desorbs as iso-alkene. The final stage of the reaction involved the hydrogenation of the latter over metallic sites to produce the desired branched paraffin (Scheme 3).

Please put scheme 3 here.

Two major difficulties with this process are the choice of the most appropriate catalyst system and length of the n-alkanes chain. With long n-alkanes, hydrocracking and/or hydrogenolysis to C_1 to C_4 may dominate the reaction if appropriate operation parameters are not selected. This reduces the amount of branched isomers formed and favor the production of much lighter unwanted hydrocarbon species, with potentials to deactivate the catalyst. Several catalysts have been evaluated in the past by the refineries. Lewis acids based on chlorides and chlorinated alumina were the early developed systems [103]. Their activities can be promoted by trace quantities of water in the feed that normally enhances Brønsted acidity through the creation of new active acid sites. However, these compounds are less stable at higher temperatures. This factor will also strongly limits any possibility with the biojet fuels-grade paraffins that will require severer conditions due to longer chain lengths. Chloride catalysts are similarly corrosive

18

with disposal difficulties [103] and [104]. Pure, doped or promoted zirconia and heteropoly acid catalysts were also tested [105] and [106]. Compounds of zirconia, especially SO_4^{2-}-ZrO_2 modified with metals, can be good hydroisomerization catalysts but posed challenges like hydrocracking of longer alkanes, decay by carbonaceous depositions, SO_4^{2-} deactivation due to interaction with hydrogen in the feed and regeneration problems. On the other hand, heteropoly acids can provide the desired acidity but are subject to quick deactivation by solvation and are of poor thermal stability. The various inconsistencies with these materials therefore attributed a shift by the refineries to zeolite-based catalysts [103],[107] and [108]. Reactions over zeolites are strongly dependent on structure-acidity properties and these are in turn critical for the hydroisomerization process. A sufficient balance between the number and strength of the acid sites and the available metal sites coupled with appropriate zeolite porosity are necessary to favor hydroisomerization over side reactions such as hydrogenolysis and hydrocracking. Metals promoted mordenite zeolites are the main catalysts given preference by industry and are usually employed at temperatures between 250 and 400°C [103] and [108]. However, the dimensional systems of these materials favor side reactions (including oligomerization and aromatization) at elevated temperatures. Researches are therefore underway to establish the most reliable catalysts.

Attempted upgrading of n-decane was recently reported by Kasian et al. [109] using germanosilicate UTL-zeolites bifunctionalized by the incorporation of 0.5wt.% Pt. Catalysts were active at temperatures lower than 300°C, producing both mono- and multiple-branched decanes. This had been attributed to high Pt dispersion of 81% and moderate zeolites acidity. Unfortunately, hydrolytic instability was encountered. UTL-zeolite catalysts deactivated rapidly in the presence of trace quantities of water. However, selectivity to multiple-branched decanes was found to increase with increased in the catalyst pore sizes. Corma et al. [110] hydroisomerized the same feedstock with 0.75 wt.% Pt supported over MCM-22, ZSM-5 and Beta zeolites at variable temperatures (190 to 250°C), 0.55 h contact time and a molar ratio of 8 (H_2/n-decane). n-Decane conversion reached 30 and 80% for the MCM-22 and ZSM-5 zeolites, respectively. However, high steric hinderance limited the production of ethyl- and mulitiple-branched decanes with ZSM-5 due to diffusion limitations associated with its pore size (0.51–0.56 nm). Pt/Beta catalyst produced the highest yields (45 to 50%) of these compounds compared to < 30% with other catalysts under comparable conversions. Reactions over all the catalysts were believed to proceed by the bifunctional mechanism described earlier, as also

19

observed by the authors in their previous work [111]. However, the 12-MR multidimensional structure of Beta zeolite and availability of active Pt particles were critical in deriving the optimal performance with this material [111]. Rapid catalyst deactivation was not prominent but hydrocracking reactions were observed forming C_5 and lighter species to greater than 40% selectivity with Pt/H-MCM-22 and Pt/H-ZSM-5 catalysts. Martens et al. [112] performed the hydroisomerization of a series of renewable n-alkanes (i.e. n-decane, n-nonadecane and pristane) using both conventionally prepared and hierarchically designed ZSM-22 zeolites. The materials were modified to achieve bifunctional catalysts by impregnation with Pt. Reactions were monitored at variable temperatures for 1 h with 1 mol% n-alkane ratio. Conversion generally increased with temperature irrespective of the feedstock nature. However, selectivity to either isomers (both mono- and multiple-branched) or cracking products was dependent on the catalyst type and feedstock nature. The n-nonadecane produced ~90% selectivity to isomers with both zeolites compared to 80 and 60% (n-decane) and 40 and 50% (pristane) for the conventional and hierarchical Pt/H-ZSM-22, respectively. Pristane was more susceptible to cracking and produced 30 and 20% cracked products for the two catalysts, respectively. Hierarchical Pt/H-ZSM-22 formed the best hydroisomerization catalyst with all the feedstocks. However, as observed by other authors [113],[114],[115] and [116], increasing the reaction temperature exerts negative effect on isomers selectivity. Zakarina et al.[117] studied the effect of metallic sites during n-hexane upgrading over acid-activated montmorillonite (MM). Three catalysts containing 0.35, 0.35 and 5 wt% of Pt, Pd and Ni loaded over MM were prepared and evaluated at 300 to 400°C, 1 bar and 0.82 h^{-1}. Increasing the reaction temperature increases the n-hexane conversion with all the materials. However, catalytic activity towards n-hexane follows the order Pt/MM>Pd/MM>Ni/MM under constant conditions. Interestingly, the maximum formation of cracking products was limited to 0.9%. However, catalysts were more selective to 2-methyl and 3-methylpentanes than multiple-branched isomers. Pt/MM and Ni/MM yield a higher amount of dibranched isomers than Pd/MM. Modification with Ni particles decreases the surface area of the parent acid-activated MM from 245 to 206 m^{2}g^{-1} but negligible effect was observed with Pt and Pd. The materials were however of comparable pore volume and pore radius ranges. The authors therefore attributed the superior activity of Pt to high dispersion of active metal sites. Hydroisomerization activities of many zeolite catalysts have been reported to strongly depend on

20

the active metals dispersion, especially when dealing with long chain hydrocarbon feeds [118],[119],[120] and [121].

Modhera et al [122] have also evaluated the effect of some other factors using similar feedstock over a Beta zeolite with 44 nm nano-size. Reactions were carried out at variable temperatures (250 to 400°C), pressures (5 to 15 bar), contact time and Pt metal loadings. Initial increase in temperature causes an overall increased in both n-hexane conversion and selectivity to isomers reaching maximum at 98%. However, at temperatures above 400°C, isomers were rapidly subjected to facile cracking. A similar trend was observed when the pressure was increased. From 0.5 to 10 bar, maximum of 72% conversion and 98% isomers selectivity were achieved. But this declined at higher reaction pressures. Contact time had a negative effects on n-hexane conversion with positive effect on isomers formation. As the contact time was raised from 0.2 to about 0.6 h, production of both methyl- and dimethyl- isomers was favored due to their increased residence time in the zeolite channels. On the other hand, increasing the metal loading from 0.25 to 2.0 wt% showed a linear increase in isomers yield up to 0.5 wt.% (corresponding to optimal yield and Pt dispersion). Any further increase caused a negative effect. The various observations were also in good agreement with previous studies [123], [124], [125].

Please insert Table 3 here.

Table 3 also presents a recent report on the activities and isomerization selectivities of some selected zeolites under variable modifications and reaction conditions. Increasing the Si/Al ratio from 11 to 26 had a pronounced effect on the activity of a 1 wt.%Pt/H-Beta catalyst. A Si/Al ratio of 16 corresponding to moderate acidity, produced the most favorable effects on both n-hexadecane conversion (30%) and selectivity to isomerization (95%) than the ratios of 11 and 26 [126]. Modification of 0.5 wt.%Pt/H-Beta with either Ca or Ba showed effect on both Brønsted acidity and activity of the parent material. Without any modification, the acidity was 94 µmol/g but decreased to 72 and 74 µmol/g when Ba and Ca were added, respectively. Interestingly, moderate acidity due to Ba modification produced the best isomers selectivity of 90% corresponding to 80% n-hexadecane conversion [127]. According to Liu et al [128], transition

21

metals such as Zn, Ce and La can also influence the activity of a 0.4 wt.%Pt/H-Beta catalyst during n-heptane upgrading. Without any modification the conversion was 51%, but rapidly decreased to 25% when modified with Zn. Interestingly, Ce and La additions shifted the n-heptane conversion to 57 and 60%, respectively. The latter materials also yielded 96% selectivity to isomers formation, corresponding to the best activity. The extent of synergism between Pt and the second metal, modification to acidity and higher dispersions were the main attributed factors. Incorporation of Al_2O_3 support into the zeolite structure can also influences the activity of a 0.3 wt.%Pt/H-MOR catalyst [129]. It could be observed that, for a 10 to 50 wt.% alumina additions, the higher the alumina loading the higher the n-heptane conversion. However, catalyst containing 30 wt.% Al_2O_3 produced the best isomers selectivity. At higher loadings, the chance of cracking due to pore-blockage is favored. Poisoning with 0.5 wt.% ethanol showed negligible effect on isomers selectivity but reduced n-heptane conversion by 5% over 0.5 wt.%Pt/H-ZSM-22 catalyst [130]. Under constant conditions, a 0.2 wt.%Pt/H-ZSM-48 catalyst yields both n-dodecane conversion and isomers selectivity that were at least five times those obtained with 0.2 wt.%Pt/H-ZSM-5. Therefore, structural effects are critical during the hydroisomerization reaction [131].

4. Conclusions

Hydrodeoxygenation (HDO) and hydrodecarboxylation (HDC) are the first steps for converting the vegetable oils into mostly n-alkanes suitable for upgrade to biojet fuels. Noble metals were the earlier catalysts to be tested and later replaced with other transition metals-based catalysts, due to many reasons including catalyst deactivation by poisoning, production of cracking species and process costs. Reaction mechanism over most of the catalyst systems proceeds by serial hydrogenation of unsaturated glycerides followed by simultaneous HDO and HDC reactions. A number of factors have been identified to affect the catalytic activity and selectivity to alkane compounds. The nature of the vegetable oil feedstock is a very critical factor. Oils with low degree of unsaturation (e.g. olive oil) are more favorable. Catalyst supports with moderate acidity like Al_2O_3 yield excellent upgrading properties at moderate reaction temperatures closer to $300^{o}C$. Modification of active metal catalyst sites by incorporation of a second or a third metal reduces the chance of catalyst deactivation, retard cracking and favor alkanes yield by

22

synergism. These properties are superior of NiMo-based catalysts even without sulfidation and at low hydrogen pressures. However, Co containing catalysts like MoCo, MoCoS could be deactivated by poisoning, fouling or loss of sulphur species. With the NiMo-based catalysts, complete conversion of vegetable oils with excellent selectivity to alkanes and suppressed side reactions can be achieved, especially when the nano-structured materials are appropriately employed. However, devoted effort is still necessary to clearly establish the actual reaction mechanism and the main active sites of each catalyst system under consideration. This can be a way forward to achieving optimal performance. Although some catalyst regeneration methods have been successfully developed, further studies are required on the strategies for handling catalyst deactivation with time.

The n-paraffins derived from vegetable oils for upgrade to high performance biojet fuels range hydrocarbons must be hydroisomerized taken into account some vital factors, particularly due to their long chain lengths compared to lighter alkanes in gasoline feed. The catalyst must be moderately acidic, because the high acidity shifts the reaction towards severe hydrocracking and consequently reduces isomers yield. The metal particles must be highly dispersed over the parent zeolites to avoid rapid hydrogenolysis and agglomeration. Zeolite catalysts promoted with Pt have so far demonstrated excellent activities. However, issues related to costs imply that cheaper metals must be explored. Other important parameters to be considered include; extreme temperature or pressure favor cracking of the isomers and decrease their overall yields, and that the metal loadings must be appropriately selected to establish a balance between active sites dispersion and acidity-structure properties of the zeolites.

Depending on the oil feedstock, n-paraffins with carbon numbers beyond the range of n-C_5 to n-C_{15} suitable for jet fuels may be produced. These compounds must first be subjected to mild hydrocracking, a process that can take place simultaneously with hydroisomerization using acidic zeolites, to produce the desired alkanes.

23

List of Tables

Table 1. Typical composition of a jet fuel (JP-4) derived from either petroleum or shale.

Table 2. Activities of some transition metal catalysts during HDO/HDC of vegetable oils.

Table 3. Recent studies on the behaviors of some modified zeolites during the hydroisomerization of a range of n-paraffinic feedstocks.

List of Figures

Figure 1. A typical operation unit for the hydrotreatment of vegetable oils in an existing refinery facility.

Figure 2. A typical block diagram for Vegan hydrotreatment and hydroisomerization of vegetable oils.

List of Schemes

Scheme 1. Schematic routes for the conversion of vegetable oil to biojet fuels via HDO/HDC and isomerization.

Scheme 2. Methanation and water-gas shift reactions that occur during HDO/HDC.

Scheme 3. Mechanism of n-paraffins/n-alkanes hydroisomerization over bifunctional catalysts (e.g. zeolites loaded with metals) using n-decane as a model compound.

24

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29

Table 1. Typical composition of a jet fuel (JP-4) derived from either petroleum or shale.

Composition	Shale-based fuel (wt.%)	Petroleum-based fuel (wt.%)
n-Alkanes (n-C_7 to n-C_{15})	68-70	40-44
i-Alkanes (straight chains)	6-10	27-32
Cycloalkanes (n- and i-)	5-7	2-4
Aromatics (benzene, toluene, xylenes etc., n- and i-)	6-10	6-12

Source: Ref.[16], [17].

Table 2. Activities of some transition metal catalysts during HDO/HDC of vegetable oils. NR = not reported.

Catalyst	Reaction conditions	Alkanes (n- and i-) yield/selectivity, %	Side reactions	Ref.
NiMoS$_2$/Al$_2$O$_3$	Palm oil, 270°C, 50 bar, 1 h^{-1}, H$_2$/oil = 1000.	28, solid products	Limited production of lighter alkanes with CO, CO$_2$.	[77]
NiMoS$_2$/Al$_2$O$_3$	Palm oil, 270°C, 50 bar, 1 h^{-1}, H$_2$/oil = 2000.	100, liquid products	None	[77]
25wt.% Ni$_2$P/SiO$_2$	Soybean oil, 150h, 3h^{-1}, 330°C, 30 bar	82	Propane and lighter species	[78]
25wt.% Ni$_2$P/H-Y	Soybean oil, 150h, 3h^{-1}, 330°C, 30 bar	78	More severe cracking	[78]

30

NiMo/Al$_2$O$_3$	Waste cooking oil, 350°C, 70 bar, 3h	99	< 1% contribution	[79]
NiMo/B$_2$O$_3$-Al$_2$O$_3$	Waste cooking oil, 350°C, 70 bar, 3h	94	About 5% contribution	[79]
CoMo/Al$_2$O$_3$	Waste cooking oil, 350°C, 70 bar, 3h	94	1.2% contribution	[79]
NiW/Al$_2$O$_3$	Waste cooking oil, 350°C, 70 bar, 3h	99	<1% contribution	[79]
2wt.% Ni over SAPO-11	Palm oil, 40 bar, 1h^{-1}, 360°C	60	10% lighter alkanes	[80]
7wt.% Ni over SAPO-11	Palm oil, 40 bar, 1h^{-1}, 360°C	67	10% lighter alkanes	[80]
9wt.% Ni over SAPO-11	Palm oil, 40 bar, 1h^{-1}, 360°C	68	14% lighter alkanes	[80]
CoMo/Al$_2$O$_3$	Vegetable oil + desulfurized petroleum diesel, 5h^{-1}, 320°C, 450h, 30bar	90	NR	[81]
NiMo/Al$_2$O$_3$	Jatropha oil, 390°C, 32.28h^{-1}	90	NR	[82]
CoMo/Al$_2$O$_3$	Jatropha oil, 390°C, 32.28h^{-1}	80	NR	[82]
NiMo/Al$_2$O$_3$	Jatropha oil, 370°C, hydrogen pressure of 35 bar and 0.9h^{-1}	80	Low production of lighter alkanes with CO, CO$_2$.	[83]

31

Sulfided NiMo/Al$_2$O$_3$	Jatropha oil, 370°C, hydrogen pressure of 35 bar and 0.9h^{-1}	81	Low production of lighter alkanes with CO, CO$_2$.	[83]
Ce (1wt.%) NiMo/Al$_2$O$_3$	Jatropha oil, 370°C, hydrogen pressure of 35 bar and 0.9h^{-1}	89	Very low production of lighter alkanes with CO, CO$_2$.	[83]
Ce (5wt.%) NiMo/Al$_2$O$_3$	Jatropha oil, 370°C, hydrogen pressure of 35 bar and 0.9h^{-1}	90	Very low production of lighter alkanes with CO, CO$_2$.	[83]
Ce (25wt.%) NiMo/Al$_2$O$_3$	Jatropha oil, 370°C, hydrogen pressure of 35 bar and 0.9h^{-1}	91	Very low production of lighter alkanes with CO, CO$_2$.	[83]
7wt.% Ni/SAPO-11	Palm oil, 320°C, 2.0h^{-1} and 40 bar	44	Low production of lighter alkanes with CO, CO$_2$.	[84]
7wt.% Ni/SAPO-11	Palm oil, 280°C, 2.0h^{-1} and 40 bar	79	Very low production of lighter alkanes with CO, CO$_2$.	[84]

32

Table 3. Recent studies on the behaviors of some modified zeolites during the hydroisomerization of a range of n-paraffinic feedstocks.

Catalyst	Conditions	Conversion, %	Isomerization selectivity/yield, %	Cracking, selectivity/ yield, %	Ref.
1wt.%Pt/H-Beta, Si/Al = 11	n-Hexadecane, 30 bar pressures, 220°C, 2h⁻¹ and hydrogen/alkane ratio = 20	24	90	10	[126]
1wt.%Pt/H-Beta, Si/Al = 16	n-Hexadecane, 30 bar pressures, 220°C, 2h⁻¹ and hydrogen/alkane ratio = 20	30	95	5	[126]
1wt.%Pt/H-Beta, Si/Al = 26	n-Hexadecane, 30 bar pressures, 220°C, 2h⁻¹ and hydrogen/alkane ratio = 20	28	77	23	[126]
0.5wt.%Pt/H-ZSM-12, Bronsted acidity	n-Hexadecane,	90	85	15	[127]

33

=94μmols/g.	295°C, 60 bars, 12 h, $1.1h^{-1}$ and a reactants ratio = 10.9				
0.5wt.%Pt/Ba/H-ZSM-12, Bronsted acidity = 72 μmols/g.	n-Hexadecane, 295°C, 60 bar, 12 h, $1.1h^{-1}$ and a reactants ratio = 10.9	90	90	10	[127]
0.5wt.%Pt/Ca/H-ZSM-12, Bronsted acidity = 67 μmols/g.	n-Hexadecane, 295°C, 60 bar, 12 h, $1.1h^{-1}$ and a reactants ratio = 10.9	86	90	10	[127]
0.4wt.%Pt/H-Beta	n-Heptane, reactants ratio = 7.9, 290°C, $2.7h^{-1}$ and 1 h.	51	82	18	[128]
0.4wt.%Pt/Zn/H-Beta	n-Heptane, reactants ratio = 7.9, 290°C, $2.7h^{-1}$ and 1 h.	25	67	33	[128]
0.4wt.%Pt/Ce/H-Beta	n-Heptane, reactants ratio = 7.9, 290°C, $2.7h^{-1}$ and 1 h.	57	96	04	[128]

34

0.4wt.%Pt/La/Beta	n-Heptane, reactants ratio = 7.9, 290°C, 2.7h^{-1} and 1 h.	60	96	04	[128]
0.3wt.%Pt/10wt.%Al$_2$O$_3$/ H-MOR	n-Heptane, 280°C, 15 bar pressure, 1h^{-1} and reactants ratio = 3.0	49	83	17	[129]
0.3wt.%Pt/30wt.%Al$_2$O$_3$/ H-MOR	n-Heptane, 280°C, 15 bar pressure, 1h^{-1} and reactants ratio = 3.0	81	74	26	[129]
0.3wt.%Pt/50wt%Al$_2$O$_3$/ H-MOR	n-Heptane, 280°C, 15 bar pressure, 1h^{-1} and reactants ratio = 3.0	97	09	91	[129]
0.5wt%Pt/H-ZSM-22	n-Heptane, 320°C, 1h^{-1}, reactants ratio = 600, 15 bar (Without poison)	85	70	30	[130]
0.5wt%Pt/H-ZSM-22	n-Heptane, 320°C, 1h^{-1}, reactants ratio = 600, 1.5MPa (0.5wt.%	80	70	30	[130]

35

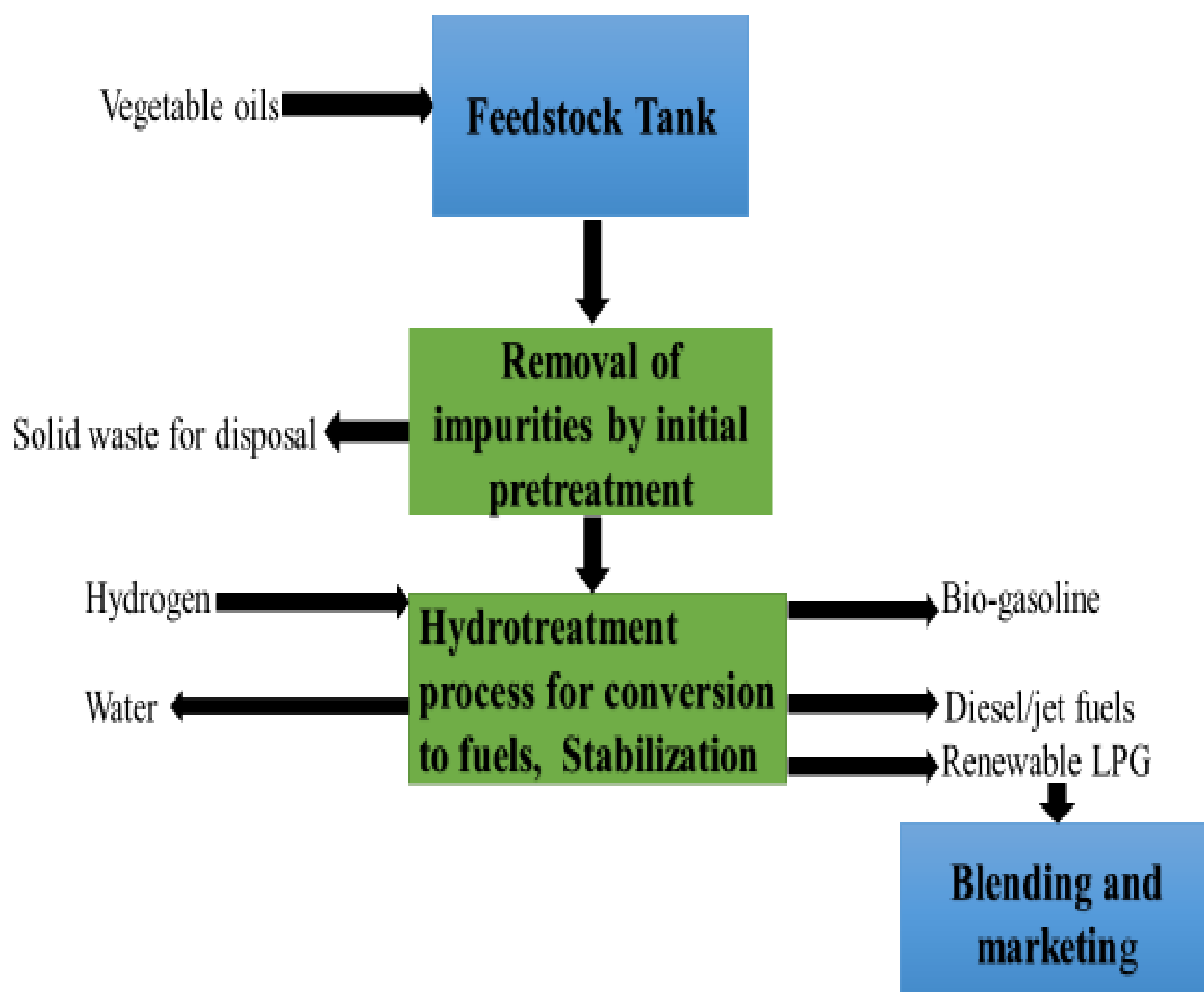|					
	ethanol as poison)				
0.2wt.%Pt/H-ZSM-48	n-Dodecane, reactants ratio = 15, space velocity of $2h^{-1}$ and $300^{o}C$	98	60	40	[131]
0.2wt.% Pt/H-ZSM-5	n-Dodecane, reactants ratio = 15, space velocity of $2h^{-1}$ and $300^{o}C$	20	10	90	[131]

36

Figure 1. A typical operation unit for the hydrotreatment of vegetable oils in an existing refinery facility.
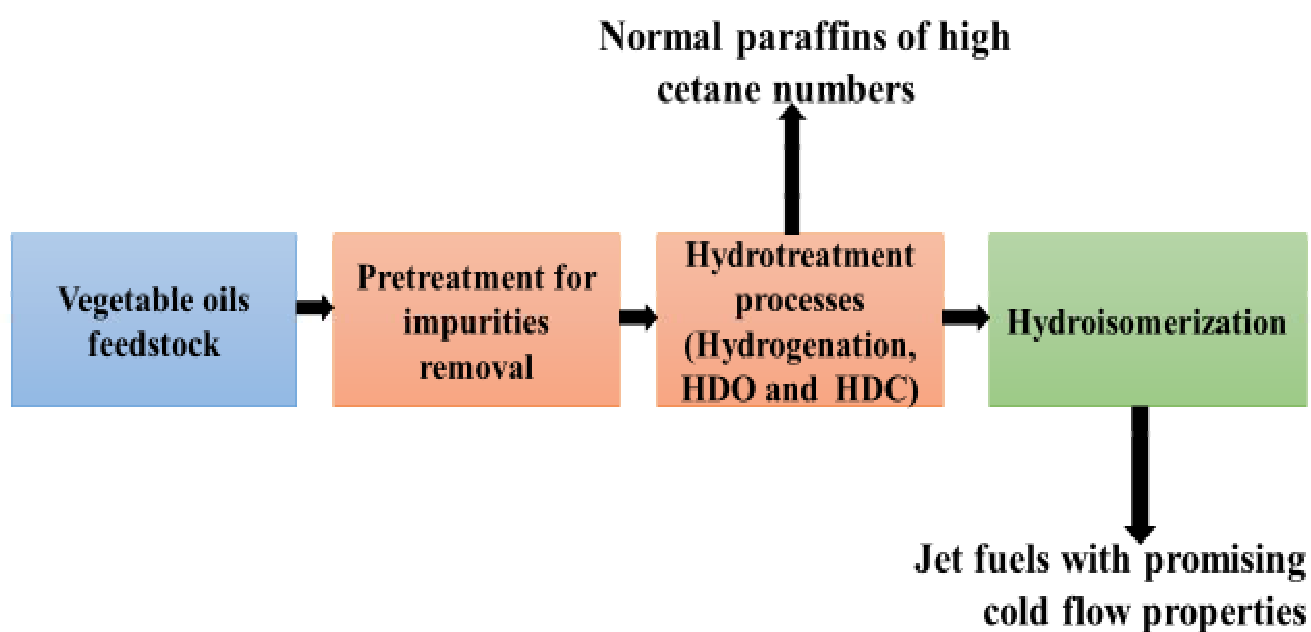
Figure 2. A typical block diagram for Vegan hydrotreatment and hydroisomerization of vegetable oils (i.e. Vegan hydrotreatment technology).

38

HDO: TGE (Vegetable oil) + xH_2 $\longleftrightarrow$ HTGE + $4xH_2$ $\longrightarrow$ n-C_zH_m + $2xH_2O$ + C_3H_8

HDC: TGE (Vegetable oil) + xH_2 $\longleftrightarrow$ HTGE + xH_2 $\longrightarrow$ n-$C_{z-1}H_m$ + xCO_2 + C_3H_8

Isomerization: n-C_zH_m $\longrightarrow$ i-C_zH_m (Biojet fuels grade)

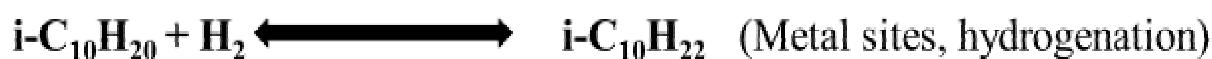n-$C_{z-1}H_m$ $\longrightarrow$ i-$C_{z-1}H_m$ (Biojet fuels grade)

Key: z, m are even numbers (m>z), x= moles of species, n = normal, i = isomer, TGE = Triglyceride ester, HTGE = Hydrogenated triglyceride ester.

Scheme 1: Schematic routes for the conversion of vegetable oil to biojet fuels via HDO/HDC and isomerization.

CO_2 + $4H_2$ $\longrightarrow$ CH_4 +$2H_2O$

CO + $3H_2$ $\longrightarrow$ CH_4 + H_2O

CO_2 + H_2 $\longrightarrow$ CO + H_2O

Scheme 2: Methanation and water-gas shift reactions that occur during HDO/HDC.

$$n\text{-}C_{10}H_{22} \longrightarrow n\text{-}C_{10}H_{20} + H_2 \text{ (Metal sites, dehydrogenation)}$$

$$n\text{-}C_{10}H_{20} + H^+ \longleftrightarrow n\text{-}C_{10}H_{21}^+ \text{ (Brønsted acid sites of zeolites)}$$

$$n\text{-}C_{10}H_{21}^+ \longleftrightarrow i\text{-}C_{10}H_{21}^+ \text{ (Brønsted acid sites of zeolites)}$$

$$i\text{-}C_{10}H_{21}^+ \longleftrightarrow i\text{-}C_{10}H_{20} \text{ (Brønsted acid sites of zeolites)}$$

$$i\text{-}C_{10}H_{20} + H_2 \longleftrightarrow i\text{-}C_{10}H_{22} \text{ (Metal sites, hydrogenation)}$$
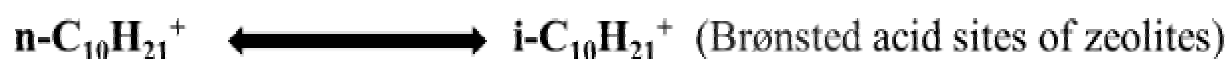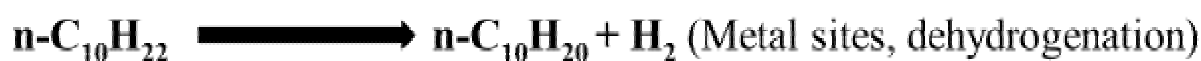
Scheme 3: Mechanism of n-paraffins/n-alkanes hydroisomerisation over bifunctional catalysts (e.g. zeolites loaded with metals) using n-decane as a model compound.

40

Normal paraffins of high cetane numbers

Vegetable oils feedstock → **Pretreatment for impurities removal** → **Hydrotreatment processes (Hydrogenation, HDO and HDC)** → **Hydroisomerization**

Jet fuels with promising cold flow properties