CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

It is worrisome that the global production of oil and gas is fast approaching its maximum due to the ever growing industrialization and technological developments which has made the demand for fossil fuel to continually be on the increase and consequently the production from large oil fields is declining at an alarming rate of 4-5% annually (Aleklett and Campbell, 2003). In view of this there will always be increasing need for substitute and renewable fuel as source of energy to meet the contemporary energy requirement. This has led the world to finding one new barrel of oil for every four it consumes because the sources of these fossil fuels will soon be exhausted (Aleklett and Campbell, 2003). Consequently, this increase in energy demand has led to an increase in crude oil price and it has drastically affected the global economic activity, politics and peace (He et al., 2010; Kovacs et al., 2011). In addition, fossil fuel is a major contributor to the dreaded greenhouse gas emissions (GHGE) that has many negative effects which include rise in the sea level, receding of glaciers, loss of biodiversity and climate change (Nigam and Singh, 2011; Du et al., 2011; Mortensen et al., 2011). This unavoidable progressing depletion of conventional fossil fuels due to the increasing energy consumption and nefarious GHGE have jointly led to a search for alternative, renewable, sustainable, efficient and cost-effective energy sources with lesser emissions (Kubickova et al., 2005; Huber et al., 2007; Lestari et al., 2008; Simakova et al., 2009; Krar et al., 2010; Du et al., 2011; Danuthai et al., 2011; Mortensen et al., 2011; Nigam and Singh, 2011; Stefanidis et al., 2011).

Thus, as an alternative to fossil fuels, first generation renewable fuel (bio-ethanol) was researched, developed and implemented in some parts of the World such as Brazil, but its reliance on food grade biomass has rendered it economically unreliable because the food requirement around the World is being compromised and the energy efficiency per unit land of the required crops is relatively low (Demirbas, 2011; Mortensen et al., 2011). In view of this, transesterification of triglycerides (fats and oils) for the production of fatty acid methyl esters (FAME) popularly referred to as biodiesel has been widely researched and improvement on the existing production techniques is still ongoing (Arend et al., 2011). However, biodiesel has certain limitations which include higher cloud point or higher viscosity compared to petroleum derived diesel and it generally has cold filter plugging points, thus it has more potential to clog the fuel filter than regular diesel fuel (Dunn, 2009; Arend et al., 2011). Other problems in biodiesel production and application include the formation of soap and hazardous wastes, problems of glycerol (by-product) disposal and marketing, high amount of unsaturated olefinic bonds which lead to poor thermal, oxidation and storage stability (Aatola et al., 2008; Balat and Balat, 2008; Jain and Sharma, 2010). In addition, there is high water content that made biodiesel to be hydrolysis sensitive which leads to corrosion problems, also worthy of note is the negative effect of phosphorus on catalytic converter (Aatola et al., 2008; Kovacs et al., 2011). In fact, the production of biodiesel with full compliance to conventional diesel is a very challenging task, therefore the search for new and cheap raw materials and alternative cheaper production techniques becomes imperative (Pinzi et al., 2009; Lapuerta et al.,2011).

As an alternative to fossil, bio-ethanol and biodiesel fuels, biofuel recently tagged Green Diesel (Arend et al., 2011) is currently being researched and have been portrayed as a future leading supplier of energy sources that have the ability to increase the security of supply, reduce the vehicle emissions and still be a good source of income to farmers (Aatola et al., 2008; Immer et al., 2010; Krar et al., 2010; Jain and Sharma, 2010; Lapuerta et al., 2011). The use of biomass waste from agriculture and forest industry to produce biofuel represents one of the less harmful but promising alternatives because it does not compete with food production and supplies or the carbon storage and the virgin value of native vegetation (Moen et al., 2009). In addition, biofuel possess hydrocarbons which are also found in conventional petroleum diesel and their properties are quite similar (Lapuerta et al. 2011). Hence, biofuel production is a promising venture to be explored to replace fossil fuels and bio-ethanol/biodiesel. Additionally, biofuel are favorable choice of fuel consumption due to its biodegradability and generating acceptable quality exhaust gases therefore they have emerged as the most strategically important sustainable fuel sources to be considered as important approach towards limiting greenhouse gas emissions and improving air quality (Moen et al., 2009; Lapuerta et al., 2011; Mortensen et al., 2011).

2.1 Different feed source for biofuel production

A number of feedstock have been researched as feed source for the production of biofuel ranging from triglycerides containing fatty acids to bio-oils obtained from the pyrolysis of solid biomass.

2.1.1 Bio-oil as feed stock

Biofuel of diesel range has been produced from bio-oil obtained via biomass gasification, liquefaction and pyrolysis processes. Among these conversion processes, pyrolysis is considered to be the most researched and promising technologies because the by-products (solid char and gases) are still valuable for further industrial applications (Wang et al., 2010). Pyrolysis is an attractive option to convert solid biomass into liquid bio-oil that is easier to manage in terms of storage, transportation and upgrade into biofuel. It is the thermal decomposition of biomass which occurs in the absence or limited quantity of oxygen than needed for complete combustion. Conventional or slow pyrolysis is defined as the pyrolysis that occurs under a slow heating rate. Fast pyrolysis (also called thermolysis) is a process in which biomass is rapidly heated to high temperatures in the absence of oxygen. A high bio-oil production requires very low vapor residence time of typically 1 s to minimize secondary reactions; although, reasonable yields can be obtained at residence times of up to 5 s if the vapor temperature is kept below 675 K (Du et al., 2011). In contrast to slow pyrolysis, fast pyrolysis is an advanced process, which needs to be carefully controlled to produce high yields of bio-oil. A typical reaction temperature of around 775 K is employed.

The bio-oil produced via pyrolysis is a viscous, corrosive, and unstable mixture of a large number of oxygenated molecules and the degree of instability which is a function of the number of oxygenated molecules depends on the pyrolysis process type and the biomass feedstock. Due to the high oxygen content, the heating value is less than half that of petroleum liquid, therefore, there is need to upgrade the liquid fuel before use. In order to improve the quality and efficiency of bio-oil production, the use of microwave-assisted pyrolysis (MAP) process has been developed and reported to offer several advantages such as uniform internal heating of large biomass particles, ease of control, and there is no need for agitation or fluidization and hence less particles (ashes) in the bio-oil as against the traditional processes (Du et al., 2011). A recent review by Mortensen et al., (2011) reported different upgrading techniques of pyrolyzed bio-oil in diesel range biofuel and the major challenges are the production of wide range of gaseous and liquid products especially olefins, esters and phenolic compounds. Wang et al., (2012) compared HDO experimental studies of both model compounds and real bio-oil derived from biomass fast pyrolysis and catalytic pyrolysis carried out over two different supported Pt catalysts. For the model compounds, the deoxygenation degree of dibenzofuran was higher than that of cresol and guaiacol over both Pt/Al_2O_3 and mesoporous Pt/MZ-5 catalyst, and the deoxygenation degree of cresol over Pt/MZ-5 was higher than that over Pt/Al_2O_3. The results indicated that HDO become much easier upon oxygen reduction. They also found out that the HDO of the real bio-oil derived from catalytic pyrolysis was much easier than that from fast pyrolysis over both Pt catalysts. Their results clearly established a synergy between catalytic pyrolysis and bio-oil hydro-processing as a good pointer towards an advanced biofuel production pathway in the future.

2.1.2 Triglycerides and fatty acids as feed stock

These appear to be the most studied group probably due to their simplified chemistry as compared to the bio-oil product obtained through pyrolysis of solid biomass. Deoxygenation of vegetable oils into hydrocarbon diesel fuel has been previously studied extensively via decarboxylation (Kubickova, et al., 2005; Pinzi 2009), and hydrotreating (Huber et al., 2007; Krar et al., 2010; Lapuerta et al., 2011). Other feed stocks that were also studied included monounsaturated fatty acid such as oleic acid (Snare et al., 2008; Arend et al., 2011), the di-unsaturated fatty acid like linoleic acid (Snare et al., 2008) and the monounsaturated fatty acid ester, methyl oleate (Snare et al., 2008). Similarly, saturated fatty acids like palmitic (Lestari et al., 2008) and stearic acid (Lestari et al., 2008; Simakova et al., 2009; Immer et al., 2010; Ping et al., 2010) have also been carefully studied and reported. Lauric (dodecanoic) acid deoxygenation under inert atmosphere into undecane (decarboxylation) and undecene (decarbonylation) paraffin has also been studied using a laboratory-scale fixed bed reactor (down-flow) and reported (Bernas et al., 2010).

Sunflower oil is a feed stock that has gained lots of attention recently, for example, Kovács et al. (2011) reported the production of biofuel by hydrotreating of triglycerides in Sunflower oil over NiMo/Al_2O_3/F catalyst. Their result showed that sun flower oil is a potential source of biofuel with a mixture of both n-paraffin and iso-paraffin. Their range of applied process parameters were temperature of 280–380 °C, total pressure 20–80 bar, liquid hourly space velocity (LHSV): 0.75–3.0 h^{-1} and H_2/sunflower oil volume ratio: 400–600 Nm^3/m^3. Similarly, Sousa et al., (2012) also reported the hydrodeoxygenation (HDO) of pure sunflower oil at a temperature and pressure of 633 K and 5 MPa, respectively to produce a biofuel in the diesel range using β-Mo_2C/Al_2O_3 as catalyst. Their catalyst was synthesized in situ using the temperature programmed carburization (TPC) methodology with a 20% (v/v) CH_4/H_2 gas mixture and 923 K/2 h as synthesis temperature. Their results showed that n-C_{18} was the major product and no CO and/or CO_2 formation were detected which implied that decarbonylation and/or decarboxylation routes do not play an important role. Kinetic studies and product profiling was also reported by Anand and Sinha, (2012) to understand the anomalous cracking of jathropha oil triglycerides in the presence of sulfided Co–Mo/Al_2O_3 catalyst. They observed only deoxygenation and oligomerization reactions between a temperature of 320 and 340 °C, whereas at temperatures above 340 °C, internal conversions between the products and direct conversion to lighter and middle distillates were favored. In their work, in order to minimize the unwanted oligomerization reaction, a high pressure of 80 bar and H_2/feed ratios >1500 were necessary and to increase the lifespan of the catalyst. The authors concluded that Jatropha oil triglycerides hydroconversion pathways were dependent on temperature and the triglycerides could be hydrocracked to lower range hydrocarbons (C_5–C_{14}) by increasing the reaction temperatures. The common observation in all these studies on the unsaturated feed stock is initial uptake of hydrogen to saturate the feed followed by deoxygenation process.

2.2 Methods of biofuel upgrading –merits and demerits

Various methods that are available for biofuel production include solvent fractionation, hydroprocessing, catalytic cracking, and decarboxylation and decarbonylation (Decarbs) reactions. The choice of any of these techniques seems to be more dependent on the available resources and facilities according the literature. The overall deoxygenation process can be described via:

1. Full saturation of double bonds (hydrogenation, if the feed is unsaturated).
2. Oxygen removal via hydrodeoxygenation (a reduction process), decarboxylation or decarbonylation reactions.
3. Removal of other heteroatoms (sulphur, nitrogen, phosphorus, metals).
4. Different side reactions such as hydrocracking of fatty acid chain of triglyceride molecule, water-gas-shift reaction, methanization, cyclization, aromatization, etc.
5. Secondary reaction like isomerization of n-paraffins which are formed during the oxygen removal (Huber and Corma, 2007).

2.2.1 Catalytic deoxygenation process via decarboxylation and decarbonylation

In decarboxylation, the production of deoxygenated fuel involves removal of oxygen molecule in the fatty acid structure as CO_2, thereby producing a linear hydrocarbon possessing one carbon less than the original fatty acid chain. Decarbonylation process is similar to decarboxylation except that it yields water and CO instead of CO_2. The advantage of this approach compared to hydrotreating is that in principle the presence of high pressures of hydrogen is not required. Immer et al., (2010) reported the deoxygenation of C_{18} fatty acids over a Pd/C catalyst and according to the reaction stoichiometry the presence of H_2 is not required for fatty acid decarboxylation process. They observed reduction in the catalyst activity due to the formation of unsaturated products which can strongly adsorb on the catalyst and thereby act as inhibitors, it was concluded in their work that the catalyst activity can be improved with the presence of H_2.

A recent study (Santillan-Jimenez et al., 2012) on the catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons through decarboxylation/decarbonylation (Decarbs) was investigated in a semi-batch autoclave over 20 wt.% Ni/C and 5 wt.% Pd/C catalysts. The obtained reaction products show that the catalyst yielded lighter products in the C_{10}–C_{17} range, the exclusion of C_{18} confirmed the formation of either or both CO and CO_2. Their study on the effect of different gases employed (N_2, 10% H_2/N_2 or H_2) showed that the presence of hydrogen resulted in improved catalytic performance and the optimum hydrogen partial pressure was found to depend on the type of catalyst used. The formation of CO is a major challenge in the Decarbs process as it gives rise to a number of phenomena affecting the catalysts performance. In the first place, any CO (a Lewis base) produced may adsorb on the catalyst surface before it can be removed from the system and this molecular adsorption in itself has the potential of inhibiting the catalysts activities (Lestari et al., 2010). It was further reported in the study on the Decarbs of triglyceride using Ni/C that when CO dissociates on Ni sites it gives rise to carbon deposits which summarily accumulated and quickly deactivate the catalyst (Santillan-Jimenez et al., 2012). Since Ni/C is indeed a high acidity catalyst, unsaturated hydrocarbons produced during the course of Decarbs reaction can in principle adsorb onto the acid sites, which may give rise to the formation of coke deposits via dehydrogenation reactions. Similarly, Arend et al., (2011) discussed the decarboxylation of oleic acid by sequential hydrogenation in hydrogen containing atmosphere (Eq. 1) and subsequent decarboxylation (Eq. 2) of the intermediately formed stearic acid. Further studies in an inert He atmosphere showed that oleic acid was mainly decarbonylated (Eq. 3) with substantially lower reaction rates to form a mixture of di-unsaturated heptadecene isomers. Conclusively, Immer et al., (2010) reported that catalysts stability will be enhanced in an H_2 atmosphere, at least by avoiding the formation of unsaturated hydrocarbon products that can adhered onto the catalyst surface and blocking the active centers of the catalyst which then prevent further reaction as earlier opined by (Santillan-Jimenez et al., 2012). Consequently, the need to explore HDO process cannot be over emphasized.

$$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35}COOH \tag{2.1}$$

$$C_{17}H_{35}COOH \rightarrow CO_2 + n\text{-}C_{17}H_{36} \tag{2.2}$$

$$C_{17}H_{33}COOH \rightarrow CO + H_2O + C_{17}H_{32} \tag{2.3}$$

2.2.2 Hydrodeoxygenation process

Catalytic HDO of carboxylic acids (in the gas phase) was demonstrated as early as 1982 when Maier et al., (1982) deoxygenated a number of carboxylic acids using heterogeneous Pd and Ni catalysts. The biofuel produced from feedstock containing triglycerides with heterogeneous catalytic hydrogenation are mainly mixtures of paraffin. In the HDO of tryglycerides and fatty acids the main products are n-paraffin with even numbers of carbon atoms (i.e. they have the same carbon number as the fatty acids of the triglyceride) unlike the generation of odd number of carbon atoms (i.e. their carbon number is lower by one than that of the fatty acid of the triglyceride molecule) observed in the Decarbs. The importance and the economical production of biofuel from triglycerides (sunflower oil containing dimethyl disulphide as sulphiding agent) using HDO was recently reported by Kovacs et al., (2011) using Ni(2.3%)Mo(13.7%)/Al_2O_3/F catalyst over process parameters range of 350–370 °C, 20–40 bar, 1.0 h^{-1} LHSV, 500 Nm^3/m^3). They reported triglycerides conversion of over 90% and the yield of the high n- and iso-paraffin (>99.9%) containing gas oil boiling range target fraction was relatively high (73.2–75.6%). However, due to the presence of C_{17} in their product stream, they concluded that during the deoxygenation of the triglycerides both HDO and the decarboxylation/decarbonylation reactions took place. In a another study on the production of biofuel in the diesel range from pure sunflower oil using β-Mo_2C/Al_2O_3 as catalyst, hydrotreatment was employed at 633 K and 5 MPa (Sousa et al.,2012). The HDO results revealed that n-C_{18} was the major product formed at the experimental conditions and that there is overall transformation of triglyceride into linear alkanes which proceeded in two steps: (i) thermal cracking of the triglyceride forming free fatty acids and (ii) hydrogenation of the double bonds and the carboxylic group of the free fatty acid forming n-alkanes. Their report showed no CO and/or CO_2 formation which implied that decarbonylation and/or decarboxylation routes do not play an important role in the study.

Earlier a study (Bezergianni et al., 2010) on the catalytic conversion of waste cooking oil into biofuel was investigated over a temperature range of (330–398 °C) during HDO process using the conventional NiMo catalysts. The authors did not only report excellent heteroatom (deoxygenation and other non-hydrocarbon) removal, but also observed that higher temperatures favor the production of iso-paraffin in the HDO process. The presence of iso-paraffins has been reported to improve the biofuel quality (Kikhtyanin et al., 2010). In view of the successes recorded in the HDO process, a number of studies (Huber et al., 2007; Aatola et al., 2008; Balat and Balat, 2008; Dunn, 2009; Krar et al., 2010; Wang et al., 2010; Lapuerta et al., 2011; Mortensen et al., 2011;

Anand et al., 2012; Sousa et al., 2012; Wang et al., 2012) have been carried out and the process has been commercialized in some countries. For example, a Two-step technology of HDO and isomerization has been commercialized by the Neste Oil at industrial scale (www.nesteoil.com). Similarly, there are three NExBTLTM plants, the first and the second were started up in Porvoo (Finland) in 2007 and 2009 with each having a capacity of 190,000 t/a and the third which was world's largest renewable diesel plant as at November 2010 came on stream in Singapore with a capacity of 800,000 t/a (Kovács et al., 2010). A similar-sized plant which is the fourth NExBTLTM plants has since been completed in Rotterdam in the Netherlands with a total initial investment cost of EUR 1.5 billion and has begun operation since mid-2011.

2.3 Hydrodeoxygenation catalysts and supports

Catalytic applications in biomass conversion and upgrading processes have involved different types of catalysts, such as activated alumina, sodium feldspar (Demiral and Sensoz, 2008) and zeolites. Other applications have employed materials such as natural zeolites clinoptinolite (Putun et al., 2006) and others synthetic ones, such as Zeolite A and MCM-41 (Wang et al., 2010).

2.3.1 Zeolite A (catalyst support)

Many studies on the use of different types of zeolites for HDO process have been widely reported. Unfortunately, the use of zeolite A in environmental and energy technology fields such as catalysis in petrochemical science, energy conservation and even air purification and wastewater treatment are restricted due to its exorbitant production cost (Hui et al,. 2009). However, recently, a novel and cheap method of Zeolite A production from Coal fly ash (CFA) which is the waste product of combustion of coal in a coal-fired power station was discovered. This discovery has hitherto brought Zeolite A into lime light since the estimated global annual production of CFA was about 800 million tons and this amount is predicted to increase in future, in addition, at present the global recycling rate of CFA is only 15% posing serious waste management challenges (Williams, 2008).

Zeolite A is a synthetic sodium aluminium silicate with the formula $Na_{12}(AlO_2)_{12}(SiO_2)_{12}.27H_20$ with Si/Al ratio of approximately 1. Its cubic microcrystals obtained from CFA shown in Figure 2.1 revealed an optimized particle shape (rounded corners and edges) and an average particle diameter of 3.5 μm. Zeolite A has a purity of $\geq$99% and trace impurities may consist of Fe_2O_3 ($\leq$ 0.2%) and amorphous alumosilicates (HERA report, 2004). It is represented by CAS Number 1344-00-9 (Sodium Aluminium Silicate) and by CAS Number 1318-02-1 (Zeolites). Its Molecular weight and melting point are 2190 g/mol and 1700 °C, respectively.

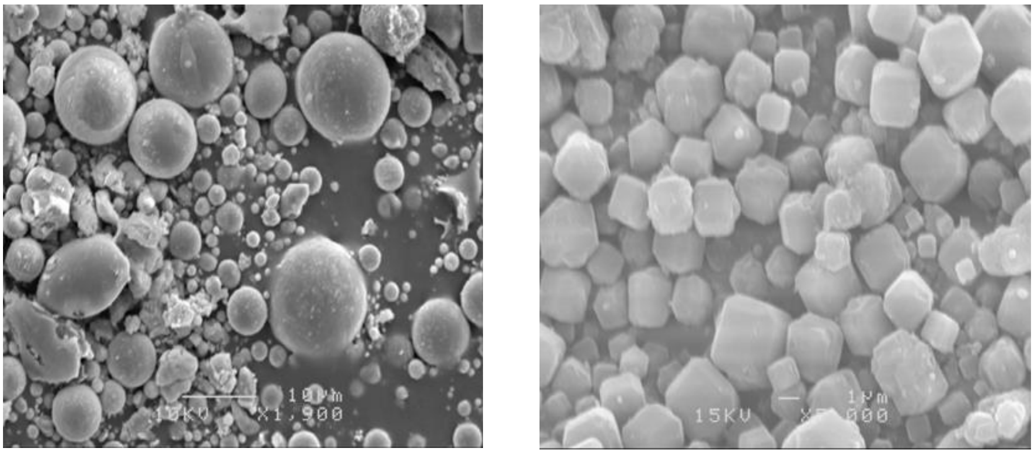

Figure 2.1 Scanning electron micrograph of Coal Fly Ash and Zeolilte A (courtesy: Hui et al., 2009)

The characteristics advantages of using Zeolite A in catalyst support include its uniform pore structure, large surface area and high thermal stability (Hui et al,. 2008).

In addition, its structure contains large cages having a near spherical shape of diameter of 11.4 Å (Hui et al,. 2009). For operations where comparably larger diameter is required such as hydrogenation or hydrodeoxygenation process, thermal and acid treatments have been recommended leading to the dealumination of its lattice structure (Figure 2.2) due to the removal of framework alumina and extra framework alumina, respectively (Panda et al., 2010; Xiaoling et al., 2012; Ayodele 2013).

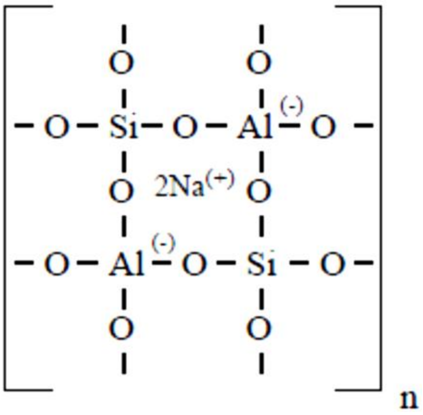

Figure 2.2 Zeolite A lattice structure

2.3.2 Alumina catalyst support

Alumina otherwise known as aluminum oxide, (Al_2O_3) commonly occurs in its crystalline polymorphic phase α-Al_2O_3, in which it comprises the mineral corundum, varieties of which form the precious gems ruby and sapphire. Its melting point, boiling point, density and molar mass are 2072 °C, 2977 °C, 3.95 g/cm^3 and 101.96 g/mol, respectively. It has two main groups, the first is high-grade alumina having at least 99% Al_2O_3 and the second is alumina grades with 80-90% Al_2O_3. Depending on different disciplines these main groups can still be further classified according to type (such as γ or α Al_2O_3), purity and intended service (Pertti, 1996). It has an internal crystal structure where oxygen ions are packed in a closed-packed-hexagonal arrangement (Figure 2.3) with aluminum (and other metals) ions in two-third of the hexagonal sites. Alumina does not easily deviate much from stoichiometry but even small levels of impurities can influence high-temperature diffusion rates greatly.

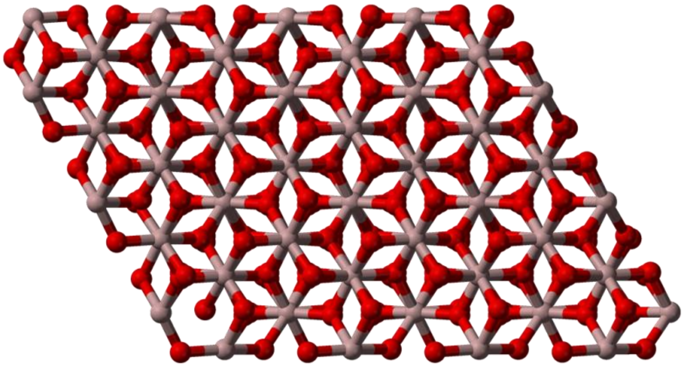

Figure 2.3 Ball-and-stick model of part of the crystal structure of α-Al_2O_3 (Pertti, 1996)

Al_2O_3 has been reported to catalyze a variety of industrially useful reactions such as the *Claus Process* for converting hydrogen sulfide waste gases into elemental sulfur in refineries and dehydration of alcohols to alkenes. Similarly, it has been used as catalyst support for many industrial catalysts, such as those used in hydrodesulfurization, hydrogen production, hydrodeoxygenation, hydrogenation and some Ziegler-Natta polymerization reactions (Ghule et al., 2009; Ghule et al., 2010; Li et al., 2012; Banget al., 2013). Since Al_2O_3 has been identified as a promising catalysts support material, it has been produced from the condensation of $Al(OH)_3$. However, the major interest has been to systematic study of $Al(OH)_3$ condensation into Al_2O_3 which was recently unraveled in a thermo-Raman spectra study of the $Al(OH)_3$ condensation forming Al_2O_3 recorded at regular temperature intervals in a dynamic thermal process from 25 to 800 ºC as shown in Figure 2.4 (Ghule et al., 2009; Ghule et al., 2010). According to Figure 2.4, typical thermo- Raman spectrum of $Al(OH)_3$ recorded at 25 ºC shows bands at 1170, 1079, 971, 890, 834, 704, 668, 535 and 429 cm^{-1} and the spectrum did not change until 400 ºC when all bands disappeared. However, at higher temperatures above 600 ºC, the bands start to reappear and become distinct at 800 ºC. A typical spectrum at 800 ºC shows bands at 1174, 1085, 1057, 1005, 916, 828, 717, 689, 600, 518, 433 and 378 cm^{-1} representing the formation of Al_2O_3.

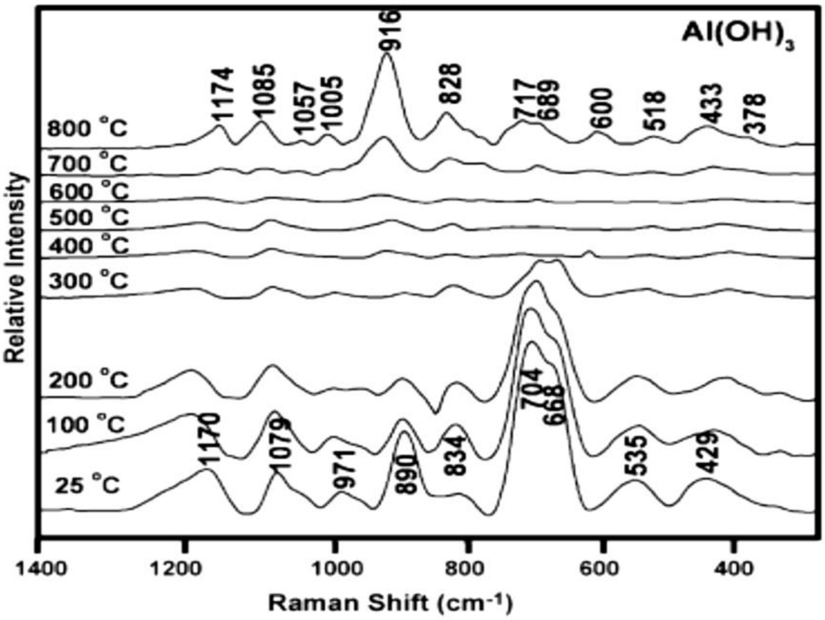

Figure 2.4 Thermo-Raman spectra (200–1400cm^{-1}) of $Al(OH)_3$ during condensation process (25–800 ºC) forming Al_2O_3, in oxygen atmosphere with heating rate of 5 ◦$Cmin^{-1}$. Courtesy: (Ghule et al., 2010).

2.4 Various synthesized catalysts for biofuel production

For hydroprocessing of various plant-derived oils, acidic supports such as amorphous mixed oxides like silica–alumina (for catalysts such as sulfided Co–Mo, Ni–Mo, Ni–W) (Kumar et al., 2010; Verma et al., 2011), phosphate modified silica-alumina (Verma et al., 2011), and crystalline acidic supports like zeolites (Huber et al., 2007; Kumar et al., 2010; Verma et al., 2011) have been successfully employed to produce cracked hydrocarbons ranging from gasoline to kerosene to diesel. The yield of cracked products increased with increasing acidity of the catalysts and since the reactions are highly exothermic, catalyst stability and selection is important (Anand et al., 2012).

Recently, a group of researchers (Kubickova et al., 2005; Simakova et al., 2009; Bernas et al., 2010; Lestari et al., 2010) have undertaken a series of studies examining the deoxygenation of fatty acids and their derivatives over supported metal catalysts. Palladium supported on activated carbon was found to be a particularly effective for the deoxygenation of fatty acids and their derivatives. In a related study (Morgan et al., 2012), the catalytic deoxygenation of triglycerides and fatty acids to hydrocarbons was investigated in a semi-batch autoclave over 20 wt.% Ni/C and 5 wt.% Pd/C catalysts. The boiling point distribution plots of the reaction products show that 20 wt.% Ni/C tends to yield lighter products in the C_{10}–C_{17} range than 5 wt.% Pd/C. The authors concluded that 20 wt.% Ni/C could be a promising catalyst to be exploited for the purposes of producing fuel blends. They also attributed the differences in the performance of the two catalysts to the higher acidity of the Ni-based formulation, which favors the adsorption of carbonaceous species and the occurrence of cracking reactions. Indeed, the high acidity of the Ni/C catalysts can give rise to a number of phenomena affecting its performance. First, any CO (a Lewis base) produced may adsorb on the catalyst surface before it can be removed from the system. The molecular adsorption of CO in itself has the potential of inhibiting the catalyst activity (Lestari et al., 2010); however, CO is also known to dissociate on Ni sites and give rise to carbon deposits, the accumulation of which can quickly deactivate the catalyst (Santillan-Jimenez et al., 2012). Moreover, unsaturated hydrocarbons produced during the course of reaction can in principle also adsorb on acid sites, which may give rise to the formation of coke deposits via dehydrogenation reactions. Since it has been previously reported that the absence of H_2 causes catalysts to suffer deactivation during triglyceride deoxygenation due to carbon deposition on the catalyst surface, this loss of activity is expected to be more severe on supported Ni catalysts compared to some other metals due to their comparatively higher acidity (Morgan et al., 2012).

In another study on the importance and economical production of the biofuel from triglycerides, Ni(2.3%)Mo(13.7%)/Al_2O_3/F catalyst was tested on the conversion of triglycerides (sunflower oil containing dimethyl disulphide as sulphiding agent). The yield product at (350–370 ◦C, 20–40 bar, 1.0 h^{-1} LHSV, 500 Nm^3/m^3) comprises of both normal and isoparaffin was over 90% containing (>99.9%) gas oil boiling range target fraction (Kovács et al., 2010). The authors concluded that during the deoxygenation of the triglycerides HDO as well as the decarboxylation/decarbonylation reactions took place since C_{17} paraffin was observed in the product stream alongside the C_{18}. The iso-paraffin content of the target product from the Ni(2.3%)Mo(13.7%)/Al_2O_3/F catalyst was significantly higher than in the product derived on non-fluorinated catalysts and thus the flow properties of the former is highly favorable in the aspect of application. Similarly, Sousa et al., (2012) also reported the hydrotreatment of pure sunflower oil at a temperature and pressure of 633 K and 5 MPa, respectively to produce a biofuel in the diesel range using β-Mo_2C/Al_2O_3 as catalyst. Their catalyst was synthesized in situ using the temperature programmed carburization (TPC) methodology with a 20% (v/v) CH_4/H_2 gas mixture and 923 K/2 h as synthesis temperature. Their results showed that n-C_{18} was the major product. The comparison of the results of the experiments without (blank) and with catalyst suggests that the overall triglyceride transformation into linear alkanes proceeds in two steps: (i) thermal cracking of the triglyceride forming free fatty acids and (ii) hydrogenation of the double bonds and of the carboxylic group of the free fatty acid forming n-alkanes. No CO and/or CO_2 formation were detected which implied that decarbonylation and/or decarboxylation routes do not play an important role when molybdenum carbide was used unlike what had been previously observed when supported Co–Mo or Ni–Mo sulfides were used (Krar et al., 2010).

Recently, Li et al., (2012) consider the possibility of one-pot method to synthesize a series of NiMo/γ-Al_2O_3 catalysts with controlled precipitation of $AlCl_3.6H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$ and $NiCO_3.2Ni(OH)_2.4H_2O$ over the traditional impregnation method to load metal oxide without washing to retain the residual chlorine from the $AlCl_3.6H_2O$. Urea and ammonium carbonate were used as additives, the molar ratio of urea to Al was varied from 4.1 to 17.2 and the influence of this variation was studied on the surface and structural properties of the catalysts. Their catalysts characterization results showed that the urea employed as additive did not only improves the solubility of Mo and Ni salt, but also adjusts the hydroxyl concentration which facilitates the formation of molybdate and polymolybdate species. The existence of residual chlorine due to non-washing of the catalyst during synthesis stage according to the authors improved the dispersion of the particles containing Ni and Mo on the surface of porous Al_2O_3 which in turn enhance hydrogen spillover and the acidity of the catalysts. The hydrometallation activity of the synthesized catalysts varied with the amount of urea to a maximum at urea/Al of 12.3 with 98% activity. They ascribed the highest activity at this ratio to better porosity, well dispersed active particles, increased octahedral molybdenum/nickel oxides and proper acidity. Their work supported the earlier claim by (Kovács et al., 2010) that acidified catalysts exhibits superior activity and can in fact produce isomerized products which are considered biofuel value-added-components.

A more complicated and advanced method of supported metal catalysts synthesis was also recently reported by Ishihara et al., (2013) where 40% of different types of zeolites and 60% alumina were mixed as NiMo catalysts composite support. The composite NiMo supported catalysts were characterized for their properties and tested for hydrocracking and isomerization of a decahydronaphthalene (decalin) solution containing 10 wt.% of 1-methylnaphthalene (1-MN) and 0.1 wt.% of dibenzothiophene. The catalysts hydrogenation activities to form methyltetralin decreased in the order NiMo/Beta(940)60A > NiMo/Beta(980)60A > NiMo/HY(5.5)60A > NiMo/USY(390)60A > NiMo/USY(360)60A > NiMo/ZSM60A at 300 °C where Beta(940) is β-zeolite with SiO_2/Al_2O_3 = 37, Beta(980) is β-zeolite with SiO_2/Al_2O_3 = 500, HY(5.5) is zeolite Y with SiO_2/Al_2O_3 = 5.5, USY(360) represents dealuminated zeolite Y with SiO_2/Al_2O_3 = 14, USY(390) represents dealuminated zeolite Y with SiO_2/Al_2O_3 = 400, ZSM-5 zeolite with SiO_2/Al_2O_3 = 1500, 60A alumina content in a composite support.

The XRD patterns of Beta(940)60A (before and after use) which is the best catalyst and that of zeolite and composited support are shown in Figure 2.5. From the patterns of Beta(940)60A, both zeolite and alumina microstructure remained in the mixed support. Even after impregnation and reaction, both peaks of zeolite and alumina indicate the maintenance of zeolite and alumina microstructure. Furthermore, no peak appears from Ni, Mo and their compounds, this according to the authors (Ishihara et al., 2013) implied that both Ni and Mo were well dispersed on the supports and no segregation of those took place in impregnation and reaction processes. Their result further elucidates that mesopore is favorable for hydrocracking and that the strength of the acid sites as well as homogeneous dispersion of metal species played an important role in the catalyst activity to have the highest yields of products.

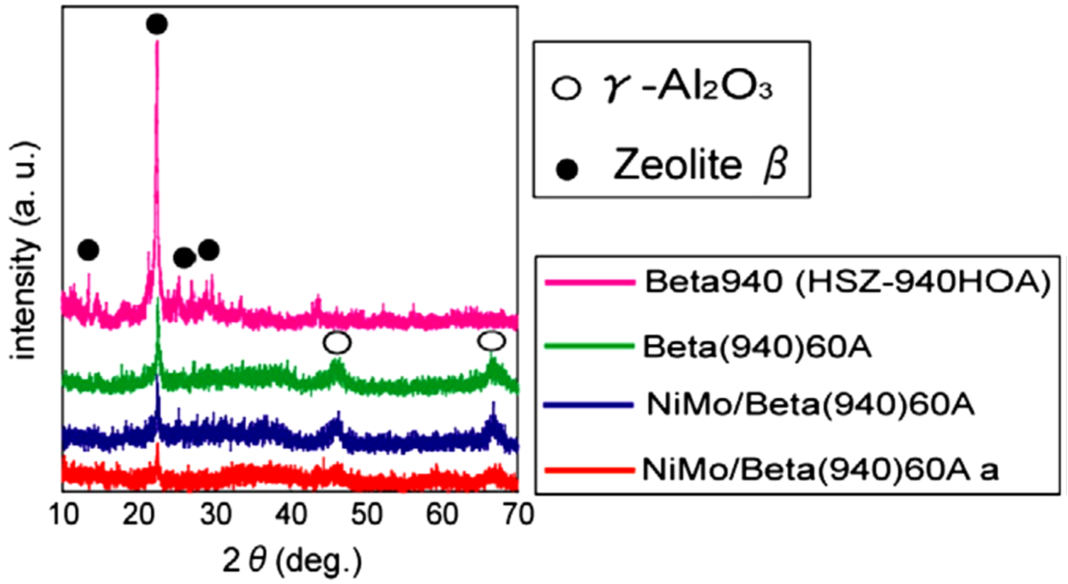

Figure 2.5 XRD patterns of zeolite, composited support, fresh and used catalysts, (a: measured after the reaction), (Ishihara et al., 2013).

The XRD patterns observed in the works of Ishihara et al., (2013) further corroborates the previous report from Bang et al., (2012) on the synthesis of ordered mesoporous nickel-alumina (OMNA) catalyst by a single-step evaporation-induced self-assembly (EISA) method. For comparison, a nickel catalyst supported on ordered mesoporous alumina support (denoted as Ni/OMA) was also prepared by an impregnation method. According to the authors (Bang et al., 2012), both Ni/OMA and OMNA catalysts retained their unidimensionally ordered mesoporous structure, but there is significant variation in their textural properties as shown in Figure 2.6 with OMNA showing increase in the pore volume due to the preparation method. Nickel species were finely dispersed in the OMNA catalyst as a form of surface nickel aluminate with a high degree of nickel-saturation (Figure 2.7). On the other hand, both bulk nickel oxide and surface nickel aluminate phases were formed in the network of Ni/OMA catalyst. Nickel species in the OMNA catalyst exhibited not only high reducibility but also strong resistance toward sintering during the reduction process, compared to those in the Ni/OMA catalyst.

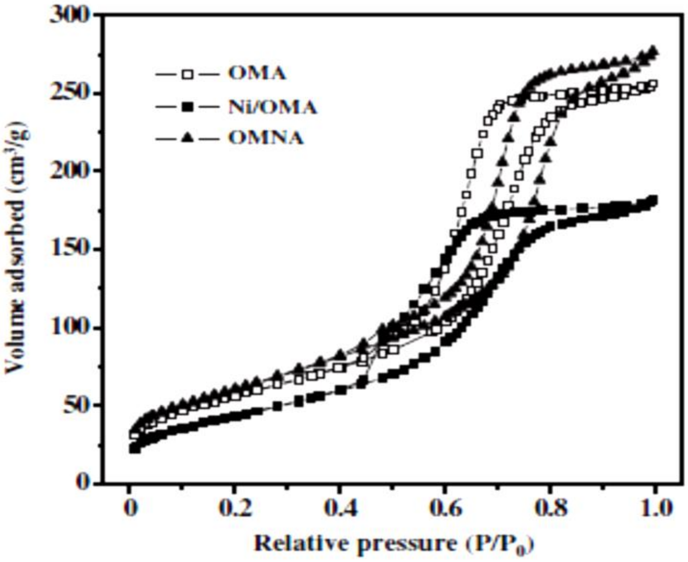

Figure 2.6 Nitrogen adsorption/desorption isotherms of support (OMA) and catalysts (Ni/OMA and OMNA) calcined at 700 ºC (Bang et al., 2012).

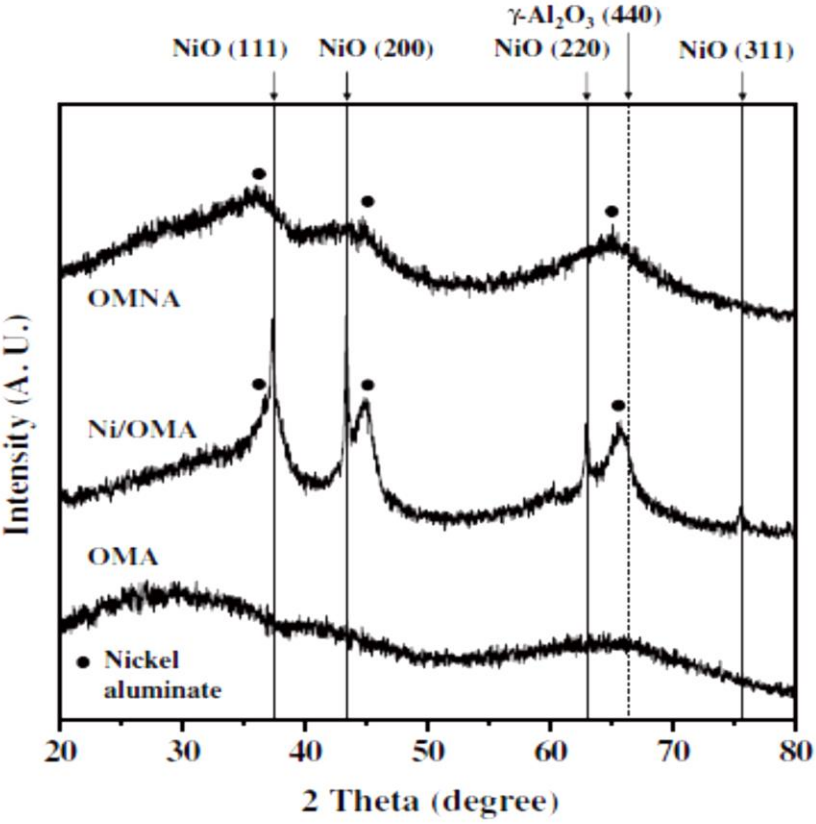

Figure 2.7 XRD patterns of support (OMA) and catalysts (Ni/OMA and OMNA) calcined at 700 ºC (Bang et al., 2012).

Table 2.1 Summary of types of catalysts employed in some of the previous works and their best observed operating conditions

s/n	Feed	Catalyst	Temp (ºC)	Pressure	Yield	References
1	rapeseed oil	sulphided NiMo/Al_2O_3				Kubicka et al., 2008.
2	Hungarian sunflower oil	NiMo/Al_2O_3/F	350–370	20–40 bar	73.2–75.6%	Kovacs et al., 2011.
3	Stearic Acid	Pd/C	270–300	17 bar	100	Lestari et al., 2008.
4	Hungarian sunflower oil	CoMo/ Al_2O_3	380	40–60 bar	(73.7–73.9%	Krar et al., 2010.
5	rapeseed oils	sulfided CoMo/γ-Al_2O_3	310	3.5 MPa	>90	Kubicka et al., 2011.
6	canola oil	5% Pd/C	300	19 bar	90% decarboxylation	Wang et al., 2012.
7	ethyl heptanoate	MoS_2 Ni_3S_2 Ni-promoted MoS_2	-	-	-	Ruinart de Brimont et al., 2012.

8	Methyl ester	CsNaX zeolites	-	-	-	Danuthaia et al., 2011.
9	C_{18} free fatty acids	5 wt% Pd/C	300	< 2 bar	98%	Immer et al., 2010.
10	Rapeseed cake and vegetable oil	Fe-ZSM-5 H-ZSM-5 H-Beta Zeolite	350-400	0.9 bar	Good Better Best	Giannakopoulou et al., 2010.
11	Triglycerides and fatty acids	20 wt.% Ni/C 5 wt.% Pd/C	-	-		Santillan-Jimenez et al., 2012.
12	Methyl-octanoate and methyl-stearate	Pt/Al_2O_3	598 K	690 kPa	~60 (C17) Decarb	Do et al., 2009.
13	Stearic Acid	2% Pd/C	300	-	95% conversion	Madsen et al., 2011.
14	Soya bean oil, Stearic acid	20 wt% Ni/C, 5 wt% Pd/C 1 wt% Pt/C	350	100 psi	-	Morgan et al., 2010.
15	methyl laurate canola oil	NiMo/γ-Al2O3	18.25-85.13	300-400	-	Kwon et al., 2011.

2.5 Effect of operational variables

Certain process variables such as reaction temperature, pressure, hydrogen and carrier gas flow rates usually affect the rate of deoxygenation process to produce biofuel.

2.5.1 Effect of reaction temperature

The effect of temperature on the deoxygenation of different feed stock has been widely studied and reported in the literature. The studied range is usually 280 – 400 °C (Kubickova et al., 2005; Huber et al., 2007; Simakova et al., 2009; Bernas et al., 2010; Lestari et al., 2010; Kumar et al., 2010; Verma et al., 2011; Anand et al., 2012; Santillan-Jimenez et al., 2012). Arend et al., studied up to 450 °C. Bezergianni et al., (2010) investigated the effect of the hydrotreating temperature over a range of 330–398 °C during the catalytic conversion of waste cooking oil as the main feedstock on conventional NiMo catalysts. From their results they observed that higher temperatures favoured the production of isoparaffin and heteroatom removal while the diesel production was favoured by lower temperatures. In other cases of co-processing (catalytic conversion of vegetable oil/gas oil mixtures) Huber et al., (2007) and Krar et al., (2010) investigated the applicability of sulphided NiMo/Al_2O_3 and sulphided NiMo/SiO_2–Al_2O_3 catalysts, respectively. They observed that the mixtures of vegetable oil and gas oil can be converted into excellent quality products with decrease in the hydrodeoxygenation and decarboxylation/decarbonylation ratio as the temperature increases. The change of the share of the different deoxygenation routes (reduction or decarboxylation/decarbonylation) as a function of the process parameters is well-characterized by the ratio of the C_{17} and C_{18} paraffin. Kovács et al., (2010) in their study concluded that the ratio of C_{18}/C_{17} paraffin decreased in the total organic products with increasing the temperature (Figure 2.8) which implied that the ratio of the decarboxylation/ decarbonylation reactions increased in correlation to the HDO on the investigated catalyst and in the applied process parameter range, their observation is in agreement with the work of Kubicka et al., (2008). Anand and Sinha, (2012) reported the kinetic studies and product profiling to understand the anomalous cracking of jathropha oil triglycerides in the presence of sulfided Co–Mo/Al_2O_3 catalyst and observed only deoxygenation and oligomerization reactions between a temperature of 320 and 340 °C. They reported that at temperatures above 340 °C, internal conversions between the products and direct conversion to lighter and middle distillates were favored. The authors concluded that Jatropha oil triglycerides hydroconversion pathways were dependent on temperature and the triglycerides could be hydrocracked to lower range hydrocarbons (C_5–C_{14}) by increasing the reaction temperatures.

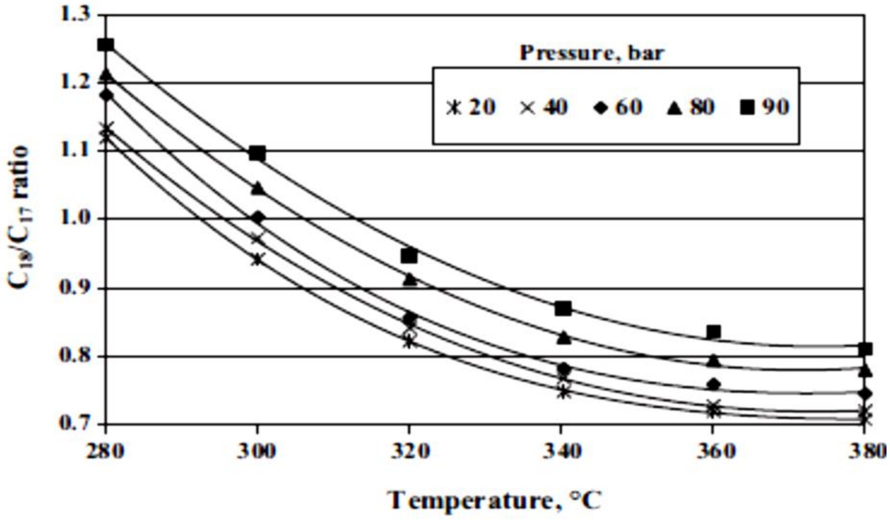

Figure 2.8 The ratio of C_{18}/C_{17} paraffins as a function of the process parameters (LHSV: 1.0 h^{-1}; H_2/sunflower oil volume ratio: 500 Nm^3/m^3) (Kovács et al., 2010).

2.5.2 Effect of reaction pressure

The effect of pressure on the deoxygenation of different feed stock has also been widely studied and reported in the literature. The studied range is usually 20–90 bar

(Kubickova et al., 2005; Huber et al., 2007; Simakova et al., 2009; Bernas et al., 2010; Lestari et al., 2010; Kumar et al., 2010; Verma et al., 2011; Anand et al., 2012; Santillan-Jimenez et al., 2012). Guzman et al., (2010) investigated the hydroprocessing of crude palm oil using a conventional hydrotreating catalyst ($NiMo/\gamma–Al_2O_3$) over a range of 40–90 bar hydrogen pressure; they obtained paraffins in the diesel range from the crude palm oil. The product mixtures contained intermediates (C_{16}–C_{18} alcohols, C_{16}–C_{18} acids and esters) and they concluded that HDO of the crude palm oil cannot be fully reached at lower pressures. Similarly, Kovács et al., (2010) in their study on the importance and economical production of the biofuel from triglycerides, $Ni(2.3\%)Mo(13.7\%)/Al_2O_3/F$ catalyst tested on the conversion of triglycerides with 20–40 bar concluded that the ratio of C_{18}/C_{17} paraffins decreased in the total organic products with decreasing pressure. Consequently, the ratio of the decarboxylation/ decarbonylation reactions increased when compared to HDO reaction. This observation is in agreement with the report of Kubicka et al. (2008) and other researcher (Lestari et al., 2010; Kumar et al., 2010; Verma et al., 2011; Anand et al., 2012; Santillan-Jimenez et al., 2012). The result of other researchers (Bernas et al., 2010) on the laboratory-scale fixed bed reactor (down-flow) for the deoxygenation of dodecanoic (lauric) acid under inert atmosphere appeared contrary. Their result studied over a range 5–20 bar showed that pressure did not have any significant impact on the performance of the Decarb process. However, this could be due to the fact that the range of pressure they studied is too comparably low. For example their upper limit of 20 bar is the same with the lower limit of other studies (Kovács et al., 2010; Krar et al., 2010). In another report (Anand and Sinha, 2012) on the kinetic studies and product profiling to understand the anomalous cracking of jathropha oil triglycerides in the presence of sulfided Co–Mo/Al_2O_3 catalyst, the authors observed both deoxygenation and oligomerization reactions in their work. In order to minimize the unwanted oligomerization reaction, a high pressure of 80 bar was necessary and to increase the lifespan of the catalyst.

2.5.3 Effect of reaction time

Although specific studies on the effect of reaction time on the process efficiency and production of biofuels are scanty in the literature, but a careful perusal and analysis of certain reported works (Kovács et al., 2010; Krar et al., 2010; Anand and Sinha, 2012) showed that the effect of time cannot be over emphasized especially when kinetic study is of essence. As a general reaction engineering rule, increase in reaction time guarantees enhanced reaction turn over, although in some cases prolong reaction time can lead to certain unwanted secondary reactions such as cracking, polymerization of already produced products as reported in some studies on the deoxygenation of different feed stocks (Kubickova et al., 2005; Kubicka et al., 2008; Simakova et al., 2009; Bernas et al., 2010; Lestari et al., 2010; Anand and Sinha, 2012)

2.5.3 Effect of catalyst loading and hydrogen gas flow

Since the hydrodeoxygenation process of oxygenated feed stocks is a catalyst dependent process, the effect of catalyst loading cannot be overemphasized. In a recent study on the Catalytic deoxygenation of oleic acid in continuous gas flow for the production of diesel-like hydrocarbons using Pd/C catalyst (Arend et al., 2011), the authors found that for low catalyst amounts (1 g) a low conversion rate of approximately 50 mol% was observed at a reaction temperature of 380 ºC and the C_{17}, heptadecane selectivity reached 18.5 mol%. However, at a higher catalyst amount of 5 g and a reaction temperature of 380 ºC, both conversion and selectivity improved, the selectivity reached its overall maximum of 28.5 mol% as shown in Figure 2.9. Similar trend was observed in other reports (Verma et al., 2011; Anand et al., 2012; Santillan-

Jimenez et al., 2012) and it was ascribed to the increase in the number of active sites available for the HDO process. Arend et al., (2011) in their study also observed that C_{17}, heptadecane was produced during deoxygenation process in the absence of hydrogen gas while C_{18}, octadecane was produced in the presence of hydrogen gas. Their observation suggests that the C_{17} and C_{18} processes followed decarbonylation/ decarboxylation and hydrodeoxygenation routes, respectively.

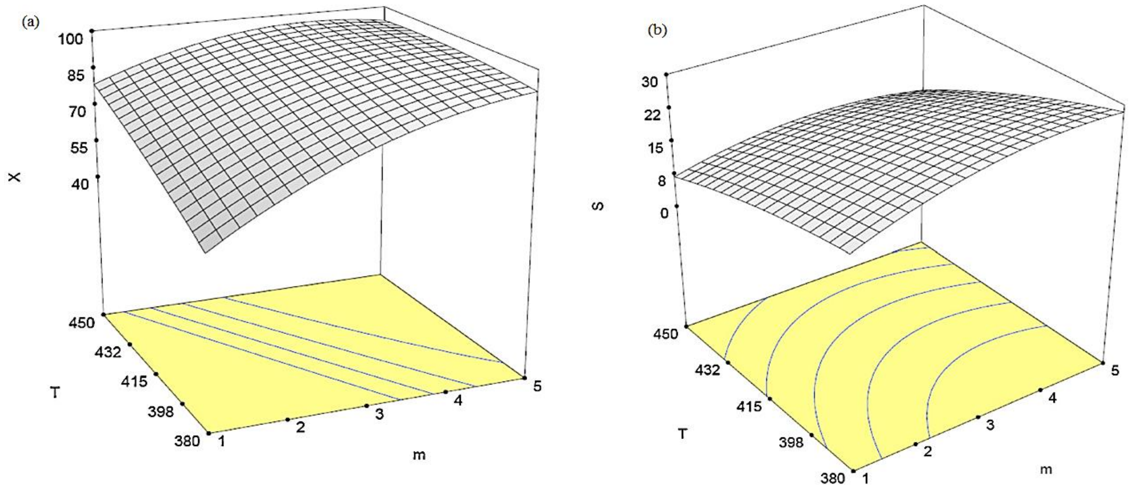

Figure 2.9 (a) Conversion (X in mol%) (b) Selectivity (S in mol%) plotted over reaction temperature (T in ◦C) and catalyst mass (m in g), V_{H2} = 50 ml/min, m_{OA} = 6.2 ml/h (Arend et al., 2011)

As a contrast to the effect of catalyst loading on the deoxygenation of oleic acid, another recent study also report the effect of NiMo/γ-Al_2O_3 catalyst in the range of 0 – 0.126 g on the HDO of 2 g methyl laurate with initial cold 46.52 – 47.90 bar hydrogen for 30 min at 350 ºC. The authors (Kwon et al., 2011) observed that the formation of hydrocarbons such as undecane and dodecane increased as the catalyst amounts increased, whereas formation of intermediate product lauric acid and unaccountable products decreased as the catalyst amounts increased as shown in Figure 2.10. Their results further showed that both catalysts and hydrogen are needed to convert methyl laurate to hydrocarbons such as undecane and dodecane. Methyl laurate is slightly converted into undecane and lauric acid in the presence of hydrogen without any catalyst loading as shown in Figure 2.10a, and hydrogen is consumed slightly in the absence of NiMo/γ-Al_2O_3 catalyst as shown in Figure 2.10b. Whereas methyl laurate is pronouncedly converted to hydrocarbons such as undecane and dodecane, lauric acid, and unaccountable by adding 0.026 g NiMo/γ-Al_2O_3 catalyst to the reaction mixture in the presence of hydrogen. The authors concluded that certain amount of the catalyst is required to ensure the formation of hydrocarbons such as undecane and dodecane, thus minimizing the lauric acid and unaccountable.

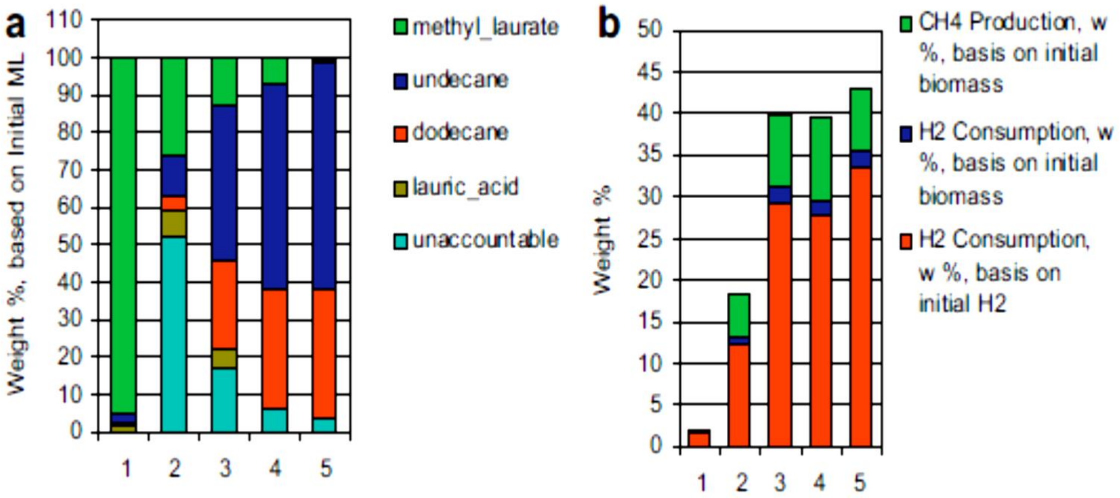

Figure 2.10 Effects of catalyst amount on liquid product distribution, H_2 consumption, and CH_4 formation, deoxidizing 2-g methyl laurate (ML) with 46.52 – 47.90 bar initial cold H_2 pressure for 30 min at 350 ºC (Kwon et al., 2011)

2.6 Isomerization products

The bio gas oils produced from feedstock containing triglycerides with heterogeneous catalytic hydrogenation are mainly the mixtures of normal-paraffins.

These product mixtures have very high cetane numbers (>85), but their cold flow properties (e.g. cold filter plugging point) are very unfavourable because of the high freezing point of the C_{16}–C_{18} n-paraffins (between 18 ºC and 28 ºC) as shown in Figure 2.11, so it is very important to improve these properties. For this purpose usually another catalytic step is recommended, which is the isomerization, because the freezing point of the isoparaffins is significantly lower than the freezing point of the n-paraffins (Kovács et al., 2010). Two-step technology such as this is used by Neste Oil in industrial scale (www.nesteoil.com). A simpler and more economical solution can be the removal of the oxygen atoms of the triglycerides and the isomerization of the n-paraffins in one step and one unit. In order to achieve this combined deoxygenation and isomerization in one step, Liu et al., (2009) developed NiMo catalysts supported on various support material (SiO_2, γ-Al_2O_3, SiO_2-Al_2O_3) and tested their activity on the catalytic conversion of jatropha oil. The NiMo/SiO_2–Al_2O_3 catalyst had the highest isomerization activity, but it had a high cracking activity as well. A good conversion and isomerization degree is achived in a study on the isomerization activity of Pd/SAPO-31 microporous catalyst on the hydroconversion of sunflower oil, although the catalyst activity dropped after 20 h due to sintering of the Pd (Kikhtyanin et al., 2010). Other authors reported the sulphidation of catalysts to achieved iso-paraffin products (Huber et al., 2007; Kubicka et al., 2008; Simácek et al., 2009; Krar et al., 2010b) and there results were promising, but the effect of sulphur is considered a threat to the environmental matrix. In view of this, Kovács et al., (2010) investigated the possibility of fluorination in a study on Ni(2.3%)Mo(13.7%)/Al_2O_3/F catalyst for the deoxygenation and isomerization of sunflower oil triglycerides. They concluded that the isoparaffin content of the Ni(2.3%)Mo(13.7%)/Al_2O_3/F catalyst was significantly higher than the products derived on non-fluorinated catalyst and thus their flow properties are favorable in the aspect of application.

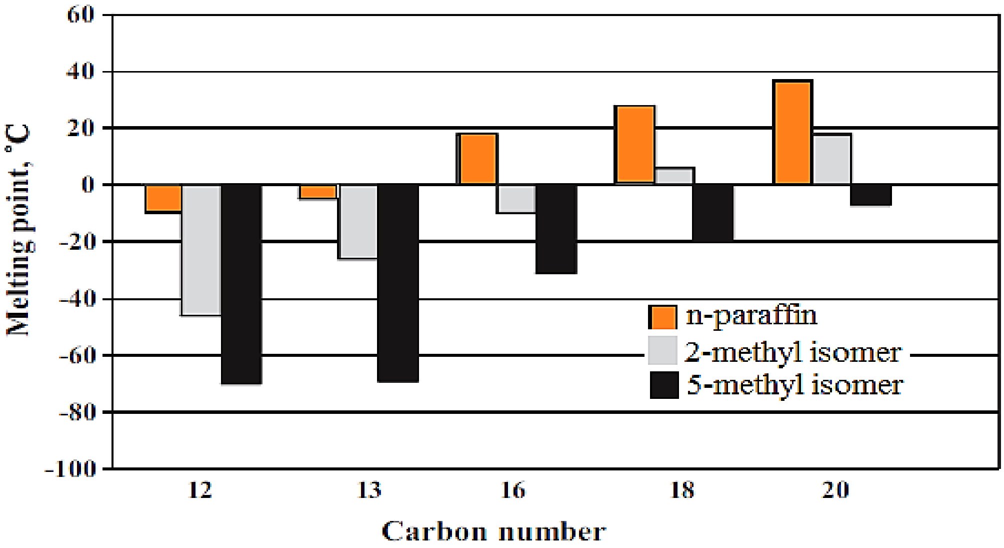

Figure 2.11 Melting points of normal and isoparaffins as a function of carbon number (Kovács et al., 2010).

2.7 Catalyst deactivation and reusability studies

Due to the poor quality of the bio-oils the conventional hydrotreating catalysts are expected to have a considerably lower catalyst life in bio-oil upgrading operations than that observed with petroleum feed-stocks. While the current generation commercial catalysts are excellent hydroprocessing catalysts they are optimized for petroleum feedstocks. Since the bio-oils have significantly different properties than petroleum feed-stocks, it would be worthwhile to dedicate efforts towards developing catalysts specifically for upgrading bio-oils. From a wide spread commercial applications viewpoint an ideal bio-oil upgrading catalyst should have the attributes described below (Choudhary and Phillips, 2011).

a) High activity for deoxygenation: this is important from the viewpoint of minimizing the reactor size and obtaining desired yields.

b) Ability to withstand large quantities of coke and/or minimize coke formation: bio-oils have a much higher propensity to form coke than typical petroleum fractions. In order to elongate the time between regeneration cycles and to achieve stable operations, the catalyst should be able to hold large quantities of coke and/or minimize coke formation.

c) High tolerance to water: previous studies have indicated that presence of water can have a detrimental effect on the deoxygenation catalyst performance (Senol et al., 2005). Since the bio-oil upgrading catalyst is expected to be exposed to large amounts of water, it is important for the catalyst to exhibit high tolerance for water. Based on the work done by Resasco et al., (2010), it may also be worthwhile to consider catalyst systems that can stabilize water-oil emulsions and catalyze reactions at the oil–water interface.

d) Ability to regenerate using a simple process such as hot air burn, this will simplify the process and minimize capital expenditure.

e) High tolerance to poisons: the activity lost due to coke deposition related deactivation can be regained during hot air burn regeneration; however activity loss from poisons is typically irreversible. High tolerance for poisons is critical from the viewpoint of increasing the overall life of the catalyst load.

One of the contemporary reports that cleverly considered many of the aforementioned points on the catalyst deactivation and reusability was contained in the studies of Kovacs et al., (2011) on fuel production by hydrotreating of triglycerides using NiMo/Al_2O_3/F catalyst (Figure 2.12). In their studies they carried out investigation of the stability of the applied catalyst on a fouling experiment which lasted 380 h, at the favorable reaction parameters (T = 350 ºC; P = 40 bar; LHSV = 1.0 h^{-1}, H_2/sunflower oil ratio = 500 Nm^3/m^3). From the results (Figure 2.12) they reported that the activity of the catalyst practically remained the same (yield of the main fraction, yield of the iso-paraffins) during the time of the whole experiment after the initial activity reduction. After the fouling experiment, the fluorine content of the catalyst taken out of the reactor changed in the limits of the analytic margin of measurement. Finally they concluded that the fluorine – despite the water forming in the reactions – did not depart from the catalyst which also confirmed that the applied catalyst has a good stability, and their results showed similarities with others report (Arend et al., 2011; Choudhary and Phillips, 2011).

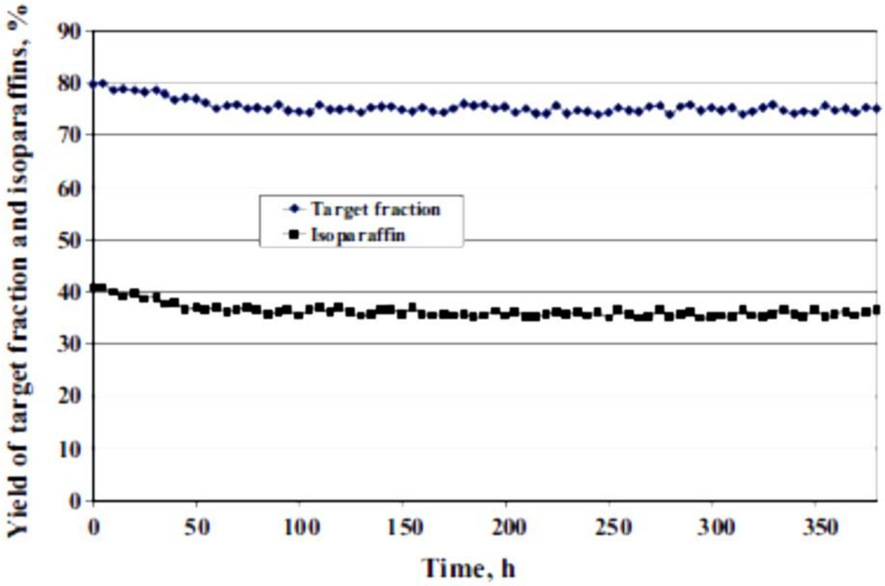

Figure 2.12 The change of the yield of the target fraction and isoparaffins during the long-term experiment on NiMo/Al_2O_3/F catalyst (T: 350 ºC; P: 40 bar; LHSV: 1.0 h−1, H_2/sunflower oil volume ratio: 500 Nm^3/m^3 (Kovács et al., 2010).

2.8 Conclusion

The surveyed literature has shown numerous contributions towards the production of green and renewable biofuel as a prospective complement and probably substitutes to the petroleum diesel. The reports showed that a large number of feed stocks have been researched and documented, similarly, a variety of catalysts have been researched, developed and tested not only for the deoxygenation process, but also for subsequent isomerization of part of the produced n-paraffins into iso-paraffins which have the ability to improve the cold flow properties of the biofuel due to its low freezing point. The general trend showed that hydrodeoxygenation process is more promising than the decarboxylation/decarbonylation processes especially when considering the issue of catalyst deactivation. On the study of the effects of process variables, high temperature seems to favor isomerization process, but there is also the tendency of cracking of the produced paraffin. Similarly, high pressure favors hydrodeoxygenation while lower pressure contributes to the decarboxylation/decabonylation process. Thorough search of the literature showed that the development of metal oxalate catalyst which could be a novel and promising deoxygenation catalyst due to its increased acidity thus capable of promoting isomerization reaction and its ability to minimize side reactions because of the coordinated metal oxalate ligand has not been reported. In addition, the investigation of the step-wise deoxygenation process based on the chemistry of the evolved products using the Fourier Transformed Infrared Spectroscopy (FTIR) has been scarcely reported. This research work is therefore aimed at bridging these gaps observed in the surveyed literature.