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Review

Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals

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Abstract

Conversion of vegetable oils and animal fats composed predominantly of triglycerides using pyrolysis type reactions represents a promising option for the production of renewable fuels and chemicals. The purpose of this article was to collect and review literature on the thermo-chemical conversion of triglyceride based materials. The literature was divided and discussed as (1) direct thermal cracking and (2) combination of thermal and catalytic cracking. Typically, four main catalyst types are used including transition metal catalysts, molecular sieve type catalysts, activated alumina, and sodium carbonate. Reaction products are heavily dependant on the catalyst type and reaction conditions and can range from diesel like fractions to gasoline like fractions. Research in this area is not as advanced as bio-oil and bio-diesel research and there is opportunity for further study in the areas of reaction optimization, detailed characterization of products and properties, and scale-up.

Keywords: Vegetable oil; Animal fat; Triglyceride; Pyrolysis; Catalytic cracking; Liquid hydrocarbon; Alkane; Renewable fuels; Renewable chemicals

1. Introduction

The majority of the world's energy is supplied by petroleum derived fuels (Brown, 2003; Royal Dutch Shell Group, 1983) and petroleum based distillates are used in a wide range of industrial applications. Petrochemicals serve as raw materials for the chemical industry in the production of solvents, lubricants, paints, and lacquers. The spectacular growth in consumption of crude petroleum during the middle and late twentieth century can be attributed to the ease with which petroleum can be discovered, produced, transported, processed, and utilized (Royal Dutch Shell Group, 1983). The oil crisis in the 1970s, depleting reserves, national scarcity issues, price uncertainty, and growing environmental concern over the combustion of fossil fuels highlight major issues associated with the extensive use of petroleum in our society. As a result, there has been renewed interest in the discovery of non-petroleum or "green" fuels and chemicals.

Alternative and renewable energy includes a wide range of technologies including wind power, solar power, hydrogen production, fuel cells, and biomass. A significant portion of renewable energy research is devoted to harnessing energy from biomass. Biomass is the only renewable energy source that yields solid, gaseous and liquid fuels (Bridgwater and Peacocke, 2000) and has been described as the renewable energy source with the highest potential to contribute to the energy needs of modern society (Bridgwater, 2003). One technique used to convert biomass into valuable liquid derivatives also known as bio-oil is pyrolysis. Pyrolysis is a severe form of thermal cracking with subsequent rearrangement of fragments (Royal Dutch Shell Group, 1983). The resulting bio-oil can then be used as fuel or for the production of chemicals and other "bio-based" products.

It is well known that triglyceride based vegetable oils or animal fats have the potential to be a suitable source of fuel or hydrocarbons under the right processing conditions. Pyrolysis of triglyceride materials is not as well established

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as other lignocellulosic biomass sources and it has been shown that these two types of bio-oils are entirely different in nature (Katikaneni et al., 1995c). The notion of vegetable oil fuels is not new. Research in this area is highly focused on the production of bio-diesel through a transesterification reaction rather than on pyrolysis. It is the intent of this review to examine the production of fuels and chemicals through pyrolysis of triglyceride based materials both with and without catalysts. The advantages and disadvantages of these processes and products in comparison to their main market competitors, bio-oils from other biomass sources and bio-diesel will also be highlighted.

2. Renewable fuels and chemicals

2.1. Conventional (petroleum derived) fuels and chemicals

Fossil fuels are the raw materials of choice for the production of fuels and chemicals. They can be easily and economically recovered and refined to produce a multitude of different products including industrial chemicals and transportation fuels. For the production of a large majority of industrial commodity chemicals, economics favor synthesis from fossil fuels. The petrochemical industry consists of seven basic building blocks: syngas from methane in natural gas and ethylene, propylene, butanes, butylenes, butadiene and BTX (benzene, toluene, and xylenes) obtained from natural gas liquids, refinery off gases, and petroleum (Brown, 2003). All organic chemicals can be derived from these building blocks. These can include products such as adsorbents, lubricants, paints, solvents, and lacquers. Petroleum derived fuels such as gasoline and diesel are also widely used as transportation fuels. Transportation needs comprise the largest single use of energy in the United States accounting for nearly 25% of total US energy consumption (Brown, 2003). Diesel and gasoline are complex mixtures consisting of numerous hydrocarbon compounds and are characterized by their properties. For renewable fuels to be successful in the market, they must have similar properties to conventional fuels. Fuel quality is measured by standardized testing methods. In the United States, these standards are governed by ASTM (American Society for Testing and Materials). The standard for diesel fuel is outlined in ASTM D975 and the standard for gasoline is outlined in ASTM D4814. There are also international standardized methods such as ISO (International Standards Organization) and European standardized methods such as CEN (European Committee for Standardization). EN 590 outlines the European guidelines for diesel fuel. Much research is focused on comparing the properties of renewable fuels with conventional fuels. This will be discussed in later sections.

2.2. The emerging bioindustry

The disadvantages associated with using petroleum for fuels and chemicals have lead to a surge in renewable energy research over the past several decades. Biomass, a naturally abundant resource, is gaining increasing recognition for its potential as a viable renewable energy source. In its broadest definition, the term biomass encompasses all natural matter of vegetables and animals (Karaosmanoglu et al., 1999) and can include a variety of natural and derived materials. It has also been described as all non-fossil based living and dead organisms and organic materials that have intrinsic chemical energy content (Klass, 2004). Today, there is a large range of bio-products available for both consumers and industry, which have been manufactured at least in part from biomass. Examples include solvents, pharmaceuticals, resins, polymers, ethanol from corn, and inks, paints, and cosmetics from vegetable oils (Paster et al., 2003). Many of these products are only partly manufactured from biomass and still contain large amounts of petroleum derived products. As biomass conversion technologies continue to advance and more bio-products enter the market, it is believed that a new "bio-industry" complete with "bio-refineries", will emerge. An extensive report on this concept as well as the status of the bio-industry has been compiled for the US Department of Energy (Paster et al., 2003).

2.3. Biomass conversion technologies

Industrial bio-products can be categorized into four major areas including (1) sugar and starch bio-products, (2) oil and lipid based bio-products, (3) gum and wood chemical (forest derivatives) based bio-products, and (4) cellulose derivatives, fibers and plastics (Paster et al., 2003). Energy can be harnessed from these biomass sources by physical, chemical, thermal, and biological methods. One of the most well known biological processes is fermentation of corn to produce ethanol. If the biomass feedstock is starch or sugar by-products, then bio-chemical conversion techniques are more common. It has recently been shown that liquid fuels in the form of longer chain alkanes can be produced from biomass carbohydrates using aqueous phase processing with acid catalysts (Huber et al., 2005). For other types of biomass feed, such as oil and lipids, forest derivatives, and cellulose derivatives, thermochemical conversion methods are preferred. Thermochemical conversion techniques represent one of the most common and convenient methods of harnessing energy from biomass. Common examples include direct combustion, gasification, liquefaction, and carbonization. These processes are described elsewhere (Bridgwater, 2003; Bridgwater and Peacocke, 2000; Brown, 2003; Paster et al., 2003). Of these thermo-chemical conversion techniques, gasification has attracted the greatest interest yet there are still drawbacks including expensive set-up, costly storage and transport of the product, and a build-up of tar in the gasification unit (Bridgwater, 2003). The products of gasification, called biosyngas, can include CO, CO_2, H_2, CH_4, and N_2. These can be used in turbines and boilers or as feed gas for the production of liquid alkanes by

Fischer–Tropsch synthesis (Boerrigter et al., 2002). The integrated biomass gasification/Fischer–Tropsch synthesis (BG–FT) approach appears promising as individually both technologies are well established, however problems exist with the combination of the technologies. One of the main problems with this approach is effective cleaning of the biosyngas prior to Fischer–Tropsch synthesis (Boerrigter et al., 2002).

Liquefaction processes result in liquid product, which can be easily stored and transported and require lower process temperatures. Due to these advantages, it is becoming increasingly evident that liquid products offer more potential for the production of bio-based products than gas products and this is reflected in the rapid development of these processes and the large amount of research in this area. Examples of liquefaction processes include high temperature pyrolysis, high pressure liquefaction, and 'ultra' or 'flash' pyrolysis. The other notable research area to mention is the production of bio-diesel through the transesterification of vegetable oils and animal fats. This is an example of a chemical process that results in a mixture of alkyl esters that can be used as a diesel fuel substitute. The production of bio-diesel as well as the pyrolysis of lignocellulosic biomass to produce bio-oil represent two major areas of renewable energy research and will be discussed further in subsequent sections. Ethanol production via fermentation is a biological method and is beyond the scope of this paper.

2.4. Pyrolytic oils from biomass

Pyrolysis is an alternative to gasification and is becoming an increasingly popular option for converting biomass to solid, liquid, and gaseous fuels. The advantages of pyrolysis include the fact that it is simple and inexpensive to construct (Onay and Kockar, 2004). The literature on pyrolysis of biomass to produce pyrolytic oils is vast and is summarized in several review articles (Bridgwater, 2003; Bridgwater and Peacocke, 2000; Yaman, 2004) and books (Brown, 2003).

The application of heat to biomass will yield pyrolytic products with gaseous, liquid, and solid fractions, the proportions of which are heavily dependent on the pyrolysis conditions. The liquid or oil fraction is commonly called pyrolytic oil or bio-oil. Slow pyrolysis, which employs lower process temperatures and longer reaction times, favors charcoal production (Bridgwater, 2003; Karaosmanoglu et al., 1999; Yaman, 2004). Currently, most research is focused on maximizing the yield of liquid product as opposed to char. The liquid pyrolytic product can be easily stored and transported, readily upgraded and refined to produce high quality fuels, and may contain chemicals in economically recoverable amounts (Karaosmanoglu et al., 1999). It can be maximized by using short residence times (generally less than a few seconds) and high heating rates (Onay and Kockar, 2004; Yaman, 2004) that characterize the fast pyrolysis method. Temperatures are approximately 500 °C (Bridgwater, 2003). A comprehensive compilation of fast pyrolysis technologies is presented by Bridgwater and Peacocke (2000).

2.4.1. Properties

Fast pyrolysis yields up to 80 wt.% liquid on dry feed (Bridgwater and Peacocke, 2000). Gaseous products consisting of aerosols, true vapors, non-condensable gases, and solid char make up the balance. The crude pyrolysis liquid or bio-oil, is dark brown in color, approximates to biomass in elemental composition and is a complex mixture of oxygenated hydrocarbons and an appreciable amount of water (Bridgwater, 2003). One of the main drawbacks of the bio-oil is that the composition of the pyrolytic oils is very similar to that of the original biomass and is very different from petroleum derived fuels and chemicals. The term biomass encompasses such a large range of feeds and therefore, the characteristics of the bio-oil can vary greatly depending on the starting material. The primary disadvantages of using the bio-oil as a diesel fuel most notably include the low HHV (Higher heating value) which is approximately 40% less than that of fuel oil, its high viscosity, and substantial solids content (Bridgwater, 2003). As well, bio-oil typically contains up to 25 wt.% water that cannot be readily separated (Bridgwater, 2003). This causes miscibility problems with conventional fuel oils and as a result, blends cannot be achieved. Pyrolysis oils have also been described as acidic, corrosive, polar, thermally unstable, and highly oxygenated (Katikaneni et al., 1995c).

2.4.2. Product applications

Bio-oil can be used as a liquid fuel or for the production of chemicals. An overview of applications of pyrolytic oils from biomass is presented in a recent review article (Czernik and Bridgwater, 2004). Fast pyrolysis has achieved commercial success for the production of chemicals and continual advancements are being made for upgrading the oils into useable transportations fuels. Pyrolysis oils can be subjected to upgrading and deoxygentation techniques such as hydrotreating and catalytic vapor cracking over zeolites to produce high grade transportation fuels (Chantal et al., 1984; Evans and Milne, 1988; Horne and Williams, 1994). The products are typically comparable to high grade gasolines and contain increased amounts of aromatics and decreased amounts of oxygen. Potential renewable chemicals from bio-oil include phenolics and cyclic ketones for resins and solvents, levoglucosan and levoglucosenon for polymers and aromatic hydrocarbons for fuel, and solvents (Elliot, 2004).

Research in the area of biomass pyrolysis is relatively advanced and there has been significant process development. Many fast pyrolysis processes are operating on a pilot or commercial scales (Bridgwater, 2003; Bridgwater and Peacocke, 2000; Elliot, 2004). Although bio-oil production from pyrolysis of biomass has been proven on commercial scale and is a very promising option for production of renewable chemicals and fuels, there are still barriers to widespread use and commercialization. These barriers are both economic and technological and are described in several articles (Czernik and Bridgwater, 2004; Elliot, 2004; Klass, 2004).

2.5. Vegetable oil (triglyceride based) fuels

Alternative feeds for the production of fuels from biomass are triglyceride based agricultural fats and oils. Fats and oils are primarily water insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (Sonntag, 1979). Vegetable oils are comprised almost completely of triglycerides and small amounts of mono and diglycerides. These materials can be pyrolyzed to produce hydrocarbon rich liquid fuels and may have the potential to supplant a fraction of petroleum based distillates and petrochemicals (Graboski and McCormick, 1998). Advantages of using vegetable oils include their liquid nature, which is convenient for transport and processing and their high heat content, which is close to 90% of diesel fuel (Karaosmanoglu, 1999). As well, vegetable oil fuels are pH neutral, contain no water, and are relatively stable (Katikaneni et al., 1995c).

The feasibility of using triglycerides as a source of energy was realized nearly a century ago when Rudolph Diesel demonstrated that vegetable oils could be used to run engines (Shay, 1993). In the past, widespread use and commercialization of vegetable oil fuels has been hindered by economics and poor properties (Knothe et al., 1997). Historically, petroleum derived fuels have been cheaper to produce. The high cost of virgin vegetable oils, which have high value in the edible oil market, is a main contributor to the overall economics of vegetable oil fuels. Recently, crude oil prices have risen to over $70 US/barrel making vegetable oil fuels, namely bio-diesel, more economically feasible. If oil prices continue to rise, bio-diesel may become economically competitive with diesel. Furthermore, if lower value oils such as waste oil or agricultural residues could be used as feedstock for bio-diesel production, economics could be improved further. A recent review on using waste cooking oil as a source for bio-diesel has recently been published (Kulkarni and Dalai, 2006). Besides economic feasibility, direct use of vegetable oils as diesel fuel has not been successful due to poor properties such as low volatility, reactivity of the unsaturated molecules, and high viscosity, which can lead to coking on engine injectors, carbon deposits, and plugged orifices during prolonged engine performance evaluations (Ali and Hanna, 1994; Demirbas, 2003a; Karaosmanoglu, 1999; Tat and Van Gerpen, 2000). Vegetable oils are suitable for diesel fuel because of their molecular structure and high energy content. Long-chain, saturated, unbranched hydrocarbons are especially suitable for diesel fuels (Knothe et al., 1997). Typically, the heat content of raw fats and oils is approximately 80–90% of No. 2 diesel fuel (Ali and Hanna, 1994; Knothe et al., 1997; Ma and Hanna, 1999). Vegetable oils represent a promising alternative fuel source if these disadvantages can be overcome, however, the properties of unprocessed vegetable oils must be significantly improved before they can be used as fuel or petrochemical feedstock. Typically, four methods are used to improve the properties of vegetable oils and fats. These methods include (1) dilution with diesel fuel or solvents, (2) microemlusification, (3) transesterification, and (4) pyrolysis (Ali and Hanna, 1994; Knothe et al., 1997; Ma and Hanna, 1999). The two most popular techniques are transesterification and pyrolysis however; the focus has been on the production of bio-diesel via transesterification.

2.6. Bio-diesel

Vegetable oils and animal fats can be transesterified to produce what is commonly referred to as bio-diesel. In past literature, the term bio-diesel has been used to describe a variety of different products including neat vegetable oils, blends of conventional diesel fuel with vegetable oils tallow and their esters or as the alkyl esters of vegetable oils and animal fats (Knothe et al., 1997). It is now formally defined as a "fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100" (ASTM D 6751-03a, 2005). These alkyl esters are produced by transesterification reactions. During transesterification, one mole of triglyceride molecules reacts with three moles of alcohol to produce a mixture of alkyl esters (bio-diesel) and glycerol. Transesterification reactions have been investigated under different reaction conditions and with a variety of catalysts including acids, bases, lipases and non-ionic bases. For commercial production, strong base catalysts such as sodium or potassium hydroxide are typically used, however alkoxide catalysts have recently gained attention because they offer some advantages over base catalysts (Knothe et al., 2005). Several reviews have been written on these subjects (Ali and Hanna, 1994; Kann et al., 2002; Knothe et al., 1997, 2005; Ma and Hanna, 1999; Pinto et al., 2005; Schuchardt et al., 1998). As with bio-oil, there is extensive bio-diesel literature available. Some excellent review articles are cited in the following sections and for further information, readers should refer to "The Biodiesel Handbook" (Knothe et al., 2005) and "Biodiesel: Growing a New Energy Economy" (Pahl, 2005).

2.6.1. Product applications

Bio-diesel is primarily used as a diesel fuel substitute or in a diesel fuel blend but it can also be used as a feedstock in the chemical industry. It is utilized in farm equipment and military vehicles and is available commercially across the United States (National Biodiesel Board, 2005). Bio-diesel also has the potential to be used for other chemical applications. They can have application as non-ionic surfactants or as emulsifying, thickening and plastifying agents (Schuchardt et al., 1998). The glycerol by-product can be sold and used in applications such as cosmetics, pharmaceuticals, food, lacquers, resins, plastics, and explosives (Schuchardt et al., 1998). However, if bio-diesel production steadily increases as expected, then glycerol will likely see a drop in value due to excess supply.

2.6.2. Properties

There are a variety of different properties which are used to assess the quality of bio-diesel. Some of these properties are the same as the properties used to assess diesel fuel quality such as combustion characteristics and cleanliness, while others pertain specifically to bio-diesel such as the glycerine content, glyceride content, iodine value and acid value. Descriptions of these properties and their importance in bio-diesel quality are described elsewhere (Knothe et al., 1997, 2005; ASTM D 6751-03a, 2005). In the US, bio-diesel standards are outlined by the in ASTM D6751. In Europe, bio-diesel standards (for use as an automotive fuel) are outlined in EN 14214 and apply to all countries that are members of the CEN. For a comprehensive list of various worldwide standards as well as descriptions of some of the important properties refer to Appendix B of The Biodiesel Handbook (Knothe et al., 2005). There have been numerous studies conducted assessing the properties of bio-diesel using different feeds and reaction parameters and comparing them to conventional diesel fuel. A comprehensive review conducted by Graboski and McCormick (1998) lists typical properties of various bio-diesels. Further information on the properties of bio-diesel can be found in extensive reviews published by Demirbas (2003b), Kann et al. (2002), Knothe et al. (1997), Srivastava and Prasad (2000) and Ma and Hanna (1999).

Typically, bio-diesel easily meets the cetane requirement for petroleum diesels, an indicator of diesel combustion and quality and can be used in a regular diesel engine with little or no modification to the existing engine. As well, many harmful emissions, which are a major concern of fossil fuel combustion, are reduced. Bio-diesel also exhibits superior lubricity to conventional diesel (Knothe and Steidley, 2005). Lubricity has recently been added to the ASTM diesel fuel standards (ASTM D975) and is becoming more of an issue because the new low sulfur diesels, required for regulatory reasons, exhibit low lubricity resulting in failure of fuel injectors and pumps (Knothe and Steidley, 2005). Another significant advantage of bio-diesel is its net positive energy balance. Life-cycle analysis of bio-diesel has shown have shown that approximately 3.2 units of fossil energy are generated for every unit of fossil energy used to produce the fuel (Sheehan et al., 1998).

Although bio-diesel shows great promise as a renewable, alternative fuel it is important to note that there are still disadvantages associated with its production and use. Bio-diesel exhibits poor cold flow properties, which can be problematic for engine performance, and increased NO_X emissions. Bio-diesel contains oxygen which may not be desirable for certain applications. The presence of oxygen lowers the heat content as shown by the heating values of bio-diesel, which are 9–13% lower than those of conventional diesel fuels on a mass basis (Demirbas, 2003a) and can also causes stability problems. It is well known that vegetable oil derivitives are prone to deterioration through hydrolytic and oxidative reactions. A comprehensive review on oxidative stability of bio-diesel is presented in Chapter 6 of The Biodiesel Handbook (Knothe et al., 2005).

Bio-oil and bio-diesel represent very promising alternative fuels, however there still are some drawbacks associated with these products that may not be desirable depending on the application. As such, there is still opportunity for development of other renewable fuels and chemicals.

3. Pyrolysis (thermal cracking) of triglycerides for fuels and chemicals

Pyrolysis or thermal cracking of triglyceride materials represents an alternative method of producing renewable bio-based products suitable for use in fuel and chemical applications. This option is especially promising in areas where the hydroprocessing industry is well established because the technology is very similar to that of conventional petroleum refining. There are significant advantages of this type of technology over transesterification including lower processing costs, compatibility with infrastructure, engines and fuel standards, and feed stock flexibility (Stumborg et al., 1996). More importantly, the final products are similar to diesel fuel in composition. The literature on pyrolysis of triglycerides was reviewed and the research was divided into catalytic and non-catalytic processes. Thermal cracking of triglycerides and fatty acid salts are discussed below and catalytic cracking is discussed in Section 4.

3.1. Triglycerides

There are several studies that have investigated the thermal cracking of triglycerides. These studies fall into two categories. One focuses on pyrolysis of model triglycerides for food science research (Crossley et al., 1962; Higman et al., 1973; Kitamura, 1971; Nawar, 1969; Nichols and Holman, 1972) while the other is devoted to cracking vegetable oils and fats for fuel applications (Adebanjo et al., 2005; Alencar et al., 1983; Chang and Wan, 1947; Dandik and Aksoy, 1998a; Egloff and Morrell, 1932; Egloff and Nelson, 1933; Fortes and Baugh, 1999, 2004; Idem et al., 1996; Lima et al., 2004; Niehaus et al., 1986; Schwab et al., 1988).

Model triglycerides including trilaurin (Kitamura, 1971), tripalmitin (Higman et al., 1973; Kitamura, 1971) and tristearin (Higman et al., 1973) have been subjected to pyrolytic conditions to determine reaction products and elucidate thermal decomposition pathways. Theses studies were mainly conducted for food science research, however reaction products were still reported. Typical reaction products included hydrocarbons, carboxylic acids, ketones, esters, and acrolein. Studies involving non-catalytic pyrolysis of vegetable oils for fuel span over the past century. Examples of early work include the cracking of cottonseed oil (Egloff and Morrell, 1932) and Alaskan fur seal oil (Egloff and Nelson, 1933). These studies were conducted at elevated temperatures (445–485 °C) and under pressure 0.93–1.3 MPa (135–200 psi) and produced between 57–60% gasoline range hydrocarbons. In 1947, motor fuels were produced from Tung oil on a large scale in response to potential fuel shortages during the war (Chang and Wan, 1947). The system was modeled after petroleum cracking processes from America and a commercial crude oil yield of 70% (v/v) of the original tung oil was reported. Twenty-five percent (volume basis) of this crude oil was reported to be gasoline. Thermal cracking was loosely categorized as (1) destructive distillation and subsequent cracking of the vapors, (2) direct thermal cracking with or without a catalyst and (3) cracking of soaps. Political and economic factors during the last three decades have resulted in a renewed interest in pyrolysis of vegetable oils for fuel production. Advances in instrumental and analytical techniques have allowed better characterization of reaction products and understanding of reaction mechanisms associated with the thermal decomposition of triglycerides.

Cracking studies have typically been carried out in batch reactors at temperatures ranging from 300–500 °C and atmospheric pressures. The organic phase of the resulting bio-oil is typically collected and analyzed. Feeds have included a range of plant and vegetable oils including tung oil (Chang and Wan, 1947), sunflower oil (Schwab et al., 1988), safflower oil (Schwab et al., 1988), canola oil (Idem et al., 1996), soybean oil (Lima et al., 2004), palm oil (Lima et al., 2004), macauba fruit oil (Fortes and Baugh, 1999, 2004), used cooking oil (Dandik and Aksoy, 1998a), castor oil (Lima et al., 2004), and various tropical vegetable oils (Alencar et al., 1983). In 1983, Alencar et al. studied the pyrolysis products of piqui, babbassu and palm oils. The cracking reactions were carried out at 300–500 °C at atmospheric pressure. The results show that the chief products were alkanes and 1-alkenes (Alencar et al., 1983). In 1988, Schwab et al. simultaneously cracked and distilled soybean and high oleic safflower oil in a destructive distillation. Seventy-seven percent of the soybean oil and 79% of the high oleic safflower oil were collected as distillates the primary products included alkanes, alkenes, aromatics, and carboxylic acids with carbon numbers ranging from 4 to greater than 20. The percentage of aromatics ranged from 1.9–2.3% and carboxylic acids from 9.6–16.1%. The fuel properties of the pyrolyzates were tested and it was found that pyrolysis resulted in products with lower viscosity and higher cetane values than the parent oil indicating that this process improved the properties of the oils. Lima et al. (2004) studied the pyrolysis of soybean, palm tree, and castor oils from 350–400 °C. The pyrolysis products were distilled into four fractions and the heavy fraction ($DT > 200$ °C) was analyzed. It was found that the pyrolysis products of the palm oil, which contains a higher percentage of saturated fatty acids, contained the largest heavy fraction. The primary products formed included hydrocarbons and oxygenated organic compounds such as alkanes, alkenes, alkadienes, and carboxylic acids. No aromatics were detected, which is contrary to previous results (Schwab et al., 1988).

The aforementioned studies were conducted in batch reactors for research purposes. Batch processes can be impractical in larger scale operations as they require clean-up and charging of the feed after each run and often experience low throughput and frequent interruptions (Idem et al., 1996). Idem et al. (1996) studied thermal cracking of canola oil in a flow type reactor over a fixed bed of inert materials. Pyrolysis was carried out between 300–500 °C at atmospheric pressure with gas hourly space velocities ranging from 3.3–640 h^{-1}. The effect of steam was also investigated. Results showed that conversions ranged between 54–100% and were heavily dependent on operating variables. The products essentially consisted of C_4 and C_5 hydrocarbons, aromatic and C_6 aliphatic hydrocarbons, and C_2–C_4 olefins as well as a diesel like fuel and hydrogen. Earlier work by the same group of researchers reported very low oil conversions (14%) and little gas production, even though the conditions and reactor were similar. Twenty-six percent of the liquid products consisted of C_6–C_{12}, non-aromatic hydrocarbons. No aromatic compounds were detected in the liquid fraction.

Many of the feeds that have been tested have high value in other markets such as the edible oil market making these processes uneconomic. Pyrolysis of waste oils may help alleviate this problem. The conversion of used cooking oil to fuel and chemical feedstock through use of a fractionating pyrolysis reactor has been investigated (Dandik and Aksoy, 1998a). Used cooking oil was fed to a special fractionating pyrolysis reactor at temperatures of 400 °C and 420 °C for approximately 180 min. The pyrolysis oil was found to contain a variety of hydrocarbons in the C_5–C_{17} including paraffins, olefins and their isomers, aromatics, cycloparaffins, and cycloolefins. It was found that it was possible to produce high concentrations of liquid hydrocarbons in the gasoline boiling range in high conversions, without the aid of a catalyst.

Most studies involving the pyrolysis of vegetable oils are generally conducted at temperature ranges between 300–500 °C with longer residence times. They do not necessarily represent true “fast or flash pyrolysis” which is generally characterized by temperatures around 500 °C and reaction times in the order of seconds. Fortes and Baugh (1999, 2004) studied the pyrolysis of macauba fruit oil under conditions more representative of fast pyrolysis. In comparison to other studies on the pyrolysis of triglyceride based oils, the temperatures were high (400–1000 °C) and the times were very short (10–30 s). The main products were found to be aldehydes, alkenes and carboxylic acids, the secondary products consisted of alkanes, cycloalkanes and unknowns.

Only recently, has literature been published involving the pyrolysis of fat instead of vegetable oil feeds. Adebanjo et al. (2005) pyrolyzed lard in a continuous microreactor loaded with different sized quartz chips at atmospheric pressure and temperatures of 600 °C and 800 °C. The lard was heated until liquefied and fed at varying flow rates with nitrogen gas. The results of the study showed that up to 61 wt.% yield of liquid product could be obtained and that a portion of this liquid fraction resembled diesel fuel.

3.2. Fatty acids and fatty acid soaps

Although the thermal cracking of triglycerides has been studied, the cracking behavior of fatty acids, a major component of the triglycerides, has not been studied extensively. In one study (Alencar et al., 1983), oleic acid was pyrolyzed, however only 11.27% (v/v) of the pyrolysis products were accounted for in the form of cycloalkanes. In a different study, the thermal decomposition behavior of stearic acid was analyzed using thermogravometric and differential thermal analysis (Jaw et al., 2001) and kinetic parameters such as activation energy were determined.

There have been some studies conducted on the thermal cracking of fatty acid salts or soaps of various oils (Chang and Wan, 1947; Demirbas, 2002; Fortes and Baugh, 1994; Hsu et al., 1950). Soaps are created via hydrolysis (saponification) of a fat with an alkali and the products include glycerin and vegetable oil soap. In the early half of the twentieth century, several studies were conducted on the thermal cracking of fatty acid soaps, however complete chemical data was not given (Hsu et al., 1950). In 1947, large scale thermal cracking of tung oil calcium soap was reported (Chang and Wan, 1947). The tung oil was saponified with lime and the calcium soap was thermally cracked to yield a diesel like fuel and small amounts of gasoline and kerosene. In a similar study, it was found that cracking the calcium salts of tung oil and stearic acid resulted in materials resembling petroleum products (Hsu et al., 1950). There were differences in the products of the two types of salts. The products from the cracked tung oil salt resulted in 41.5% cracked distillate and 48% coke, while the cracked of stearic acid salts resulted in a higher yield of distillate (76.0%) and a much lower yield of coke (17.3%). From this data, reaction mechanisms were proposed. More recently, Fortes and Baugh (1994) developed a method for analyzing calcium soap pyrolysates for hydrocarbon, ketone and aldehyde fractions. They found that aside from the presence of some ketones, the organic phase of the pyrolysates had similar composition to diesel fuel.

These studies show that high conversions and reasonable yields of diesel like fuel can be obtained from direct thermal cracking of triglycerides. There are still undesirable, oxygenated compounds present in the products and thus researchers' focus has shifted to catalytic cracking to increase conversion and liquid yield and to improve product properties.

3.3. Reaction mechanisms

There have been studies conducted on the decomposition of both saturated and unsaturated triglycerides during the applications of heat (Crossley et al., 1962; Higman et al., 1973; Kitamura, 1971; Lipinsky et al., 1985; Nawar, 1969). It is well recognized that at 300 °C the gross pyrolysis of fats results in the formation of fatty acids and acrolein. At higher temperatures, (400–500 °C) cracking occurs, producing short chain hydrocarbons (Crossley et al., 1962).

The mechanisms involved thermal cracking of saturated triglycerides have been studied (Alencar et al., 1983; Chang and Wan, 1947). Chang and Wan (1947) proposed a reaction scheme for the pyrolysis of saturated triglycerides, which includes 16 types of reactions and is shown in Fig. 1. It is believed that the larger part of the acids, acrolein, ketenes formed in Eq. (1) are rapidly decomposed according to Eqs. (2) and (3) and that Eqs. (6) and (11) are chiefly responsible for the formation of hydrocarbons constituting liquid fuels, especially in the gasoline fraction. Based on the scheme proposed by Chang and Wan (1947) and on results by Greensfelder et al. (1949), Alencar et al. (1983) also proposed a scheme for the cracking of saturated triglycerides. The scheme is presented in Fig. 2. The cracking of the triglyceride produces free radicals (A) $RCOO^{\bullet}$ and (B) $RCH_2O^{\bullet}$. The odd *n*-alkanes and 1-alkenes are formed by decarboxylation of Radical (A) and then by subsequent disproportionation and ethylene elimination. The even series of alkanes and alkenes are produced by the loss of a ketene from radical (B) and followed again by disproportionation and ethylene elimination.

Because plant oils also contain unsaturated components, it is useful to study the impact of heat on unsaturated fatty acids. In 1988, Schwab et al. proposed a mechanism (Fig. 3) to account for the formation of alkanes, alkenes, alkadienes, aromatics and carboxylic acids from the pyrolysis of unsaturated triglycerides. Generally, the thermal decomposition of these structures proceeds through either a free radical or carbonium ion mechanism as previously proposed and generally follows the Rice free radical theory modified by Kossiakoff (Alencar et al., 1983). The formation of alkanes and alkenes can be attributed to the generation of an $RCOO^{\bullet}$ radical through triglyceride cleavage followed by decarboxylation. Unsaturated sites enhance cleavage at the C–C double bond, at a position α, β to the unsaturation and this cleavage is a dominant reaction. The formation of aromatics is supported by Diels–Alder ethylene addition of a conjugated diene and carboxylic acids are most likely formed through cleavage of the glycerol moiety as suggested by Nawar (1969). This also results in the formation of acrolein, which was also detected in the pyrolysis of sunflower oil (Schwab et al., 1988).

In reality, vegetable and plant oils contain a complex mixture unsaturated and saturated triglycerides. Idem et al. (1996) studied the thermal cracking of canola oil in the presence and absence of steam and postulated a reaction scheme to account for the thermal cracking of both

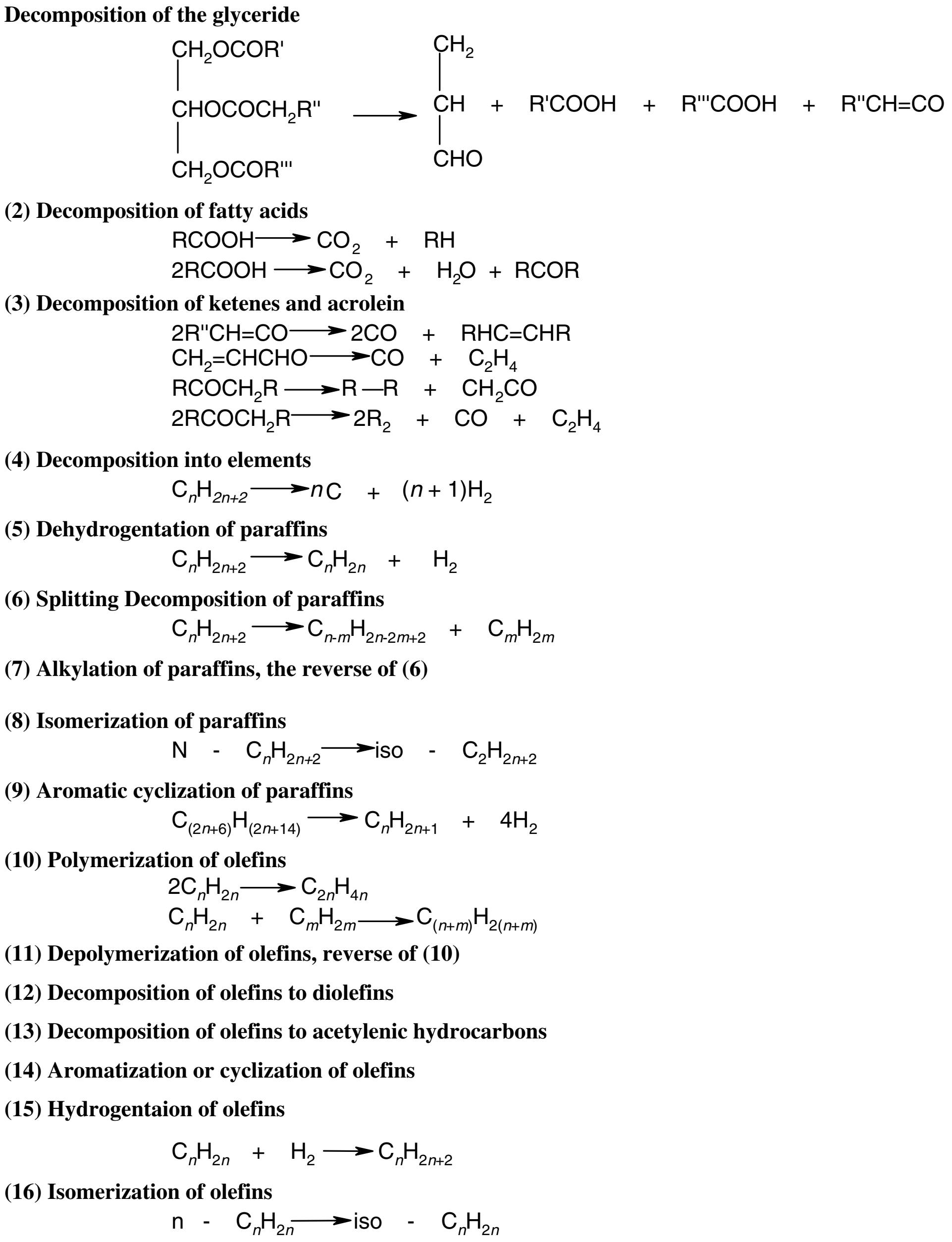

Fig. 1. Decomposition of triglycerides (Chang and Wan, 1947).

the unsaturated and saturated components. This scheme is more complex but builds on mechanisms previously proposed (Alencar et al., 1983; Chang and Wan, 1947; Kitamura, 1971; Nawar, 1969; Nichols and Holman, 1972; Schwab et al., 1988). The reaction scheme is shown in Fig. 4 and accounts for the formation of heavy oxygenated compounds including ketones, aldehydes and esters, carbon monoxide and carbon dioxide, C_1–C_5 straight and branched chain hydrocarbons, alcohols and dimethyl ether, diolefinic, cyclic and acetylenic hydrocarbon gases, C_6+ aliphatic hydrocarbons, aromatics, heavy hydrocarbons, coke, and hydrogen during the cracking of canola oil in the absence of a catalyst. The degree of unsaturation of the triglyceride has a significant effect on the cracking behavior. For example, the radical intermediates that will eventually react to form C_1–C_5 hydrocarbons can be produced via the decomposition of the heavily oxygenated compounds by different routes. Decarboxylation and decarbonylation can occur before or after the C–C bond cleavage. If the triglyceride is unsaturated, the cleavage most likely occurs before the decarboxylation and decarbonylation. It has also been shown that C–C bond cleavage for unsaturated and saturated molecules results in different products (Idem et al., 1996).

These studies show the complexity of pyrolysis reactions and possible products. Cheng et al. (2004) recog-

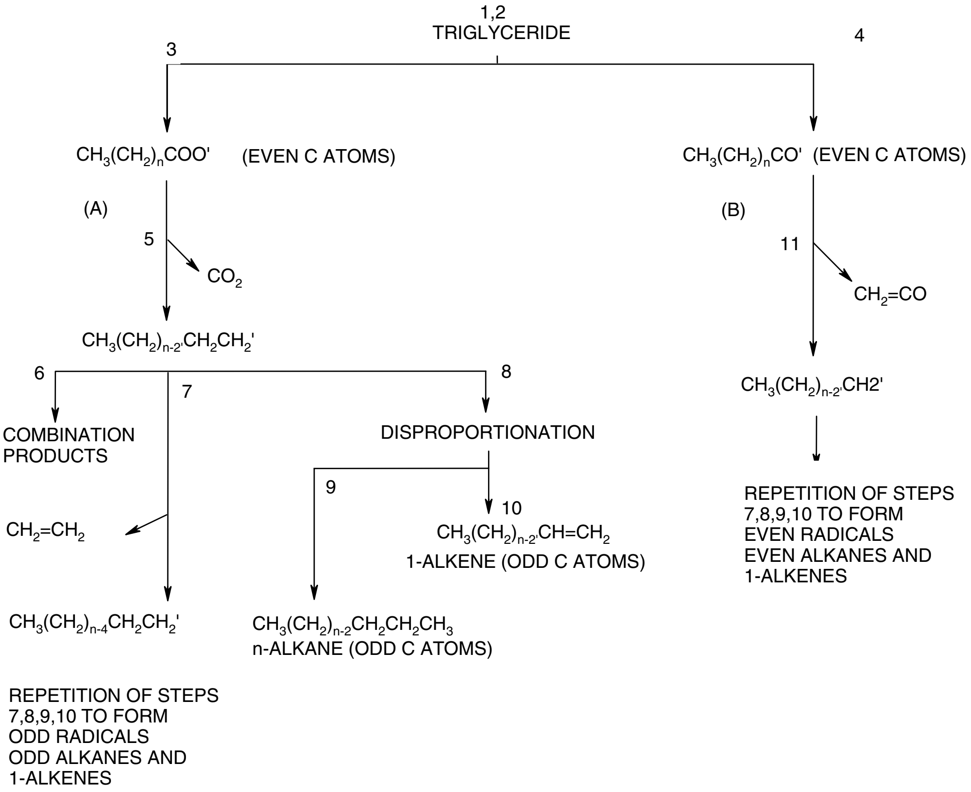

Fig. 2. Reaction mechanism for the pyrolysis of saturated triglycerides (Alencar et al., 1983).

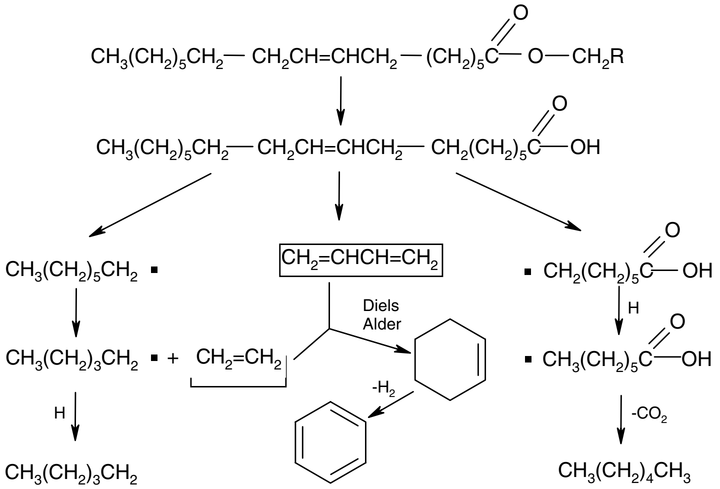

Fig. 3. Reaction mechanism for the pyrolysis of triglycerides (Schwab et al., 1988).

nized that historical studies have often neglected the possible control measures needed to form ideal products by selecting proper pyrolysis temperatures and conditions. In an attempt to better understand the pyrolysis of vegetable oils this research group studied the thermodynamics of vegetable oil process by computer simulation. The main findings were that cleavage of the C–O bond takes place at 288 °C and that scission of C=C takes place at 400 °C.

4. Catalytic cracking of triglycerides for fuels and chemicals

In most studies involving the conversion of triglycerides into hydrocarbons at high temperatures, a catalyst is used and there is a rich body of literature in this area. A comprehensive list of early studies using a variety of different catalysts is listed in US Patent 4,102,938 (Rao, 1978). Over the past several decades a variety of conventional hydrotreating catalysts have been studied in the conversion of triglyc-

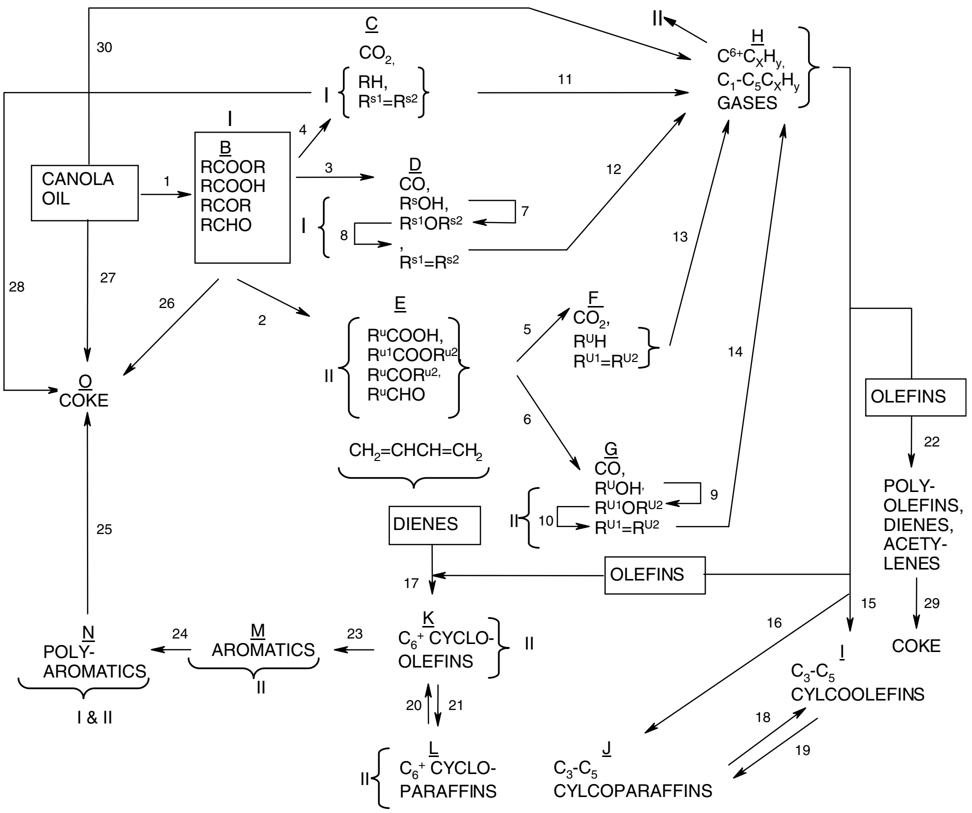

Fig. 4. Reaction mechanism for the pyrolysis of saturated and unsaturated triglycerides (Idem et al., 1996).

eride materials to fuels. The two major groups of catalysts used include transition metal catalysts which are common in the hydroprocessing industry and molecular sieve type catalysts. The use of transition metal catalysts under high hydrogen partial pressures result in diesel like products which molecular sieve catalysts result in highly aromatic, gasoline type products. Pure insulator oxides, most notably activated alumina, and sodium carbonate represent two other groups of catalysts that have been used for these applications and will also be discussed.

4.1. Activated alumina

Pure insulator oxides including MgO, SiO_2 and Al_2O_3 represent an important group of catalysts. In their pure state they are not notably acidic and there main activity is dehydration (Campbell, 1983). Alumina (Al_2O_3) can exist in several forms and depending on preparation method and treatment it can become activated (acidic) meaning it shows high catalytic activity. A common alumina catalyst is γ-alumina which is prepared by heating and evaporating the water of a trihydrate initially formed by hydrolysis of sodium aluminate (Campbell, 1983). It has been shown that activated alumina is an effective catalyst for decarboxylation of fatty acids at atmospheric pressure and 450 °C (Vonghia et al., 1995) and has been used in a series of studies investigating the production of alkanes and alkenes from sewage sludge that contains triglycerides (Boocock et al., 1992a,b). Trinolein, canola oil, trilaurin and coconut oil were pyrolysed over activated alumina at 450 °C under atmospheric pressure and the liquid products yields ranging from 65–79% were found to be hydrocarbon mixtures containing *n*-alkanes and *n*-alkenes. Elemental composition showed an absence of oxygen. Subsequent studies from the same group of researchers yielded similar results (Konar et al., 1994). Dos Anjos et al. (1983) showed that at temperatures of 300–350 °C crude and hydrogenated soya oil pyrolyzed over MgO and alumina resulted in only partial conversion to hydrocarbons. The products contained approximately 50% carboxylic acids and 25–28% hydrocarbons (Dos Anjos et al., 1983). Activated alumina is one of the catalysts used for cracking a range of vegetable oils in US Patent 5,233,109 (Chow, 1993). In this patent it was found that the products which consisted of gaseous and liquid hydrocarbons, water and coke, that suitable fuel fractions could only be obtained with further fractional distillation.

4.2. Molecular sieve catalysts

Molecular sieve catalysts are highly crystalline and porous and exhibit size selectivity. This means that only molecules of a certain size can pass through and therefore, aside from being highly reactive the pore size can be altered to obtain specific reaction products. There have been many studies that have used zeolite catalysts for conversion of triglyceride based oils and fats to hydrocarbons (Dandik et al., 1998; Katikaneni et al., 1995a,b,c, 1996; Prasad et al., 1986a,b; Sang et al., 2003, 2004; Twaiq et al., 1999, 2004; Weisz et al., 1979). Zeolite catalysts are crystalline alumino-silicate materials based on a three dimensional network of AlO_4 and SiO_4 tetrahedrally linked through oxygen atoms (Campbell, 1983). Their crystalline structure and tetrahedral shape offers significant advantages over amorphous silica–alumina catalysts. Localized regions of high electrostatic field associated with the presence of cations are highly reactive. This enhances catalytic activity and thus increases cracking. Pore size can be altered depending on what molecules are to be cracked and what reaction products are desired. When considering hydrocarbon cracking, an important zeolite catalyst is the ZSM-5. It is synthetic and its basic structure consists of layers of silica–alumina pentagon chains linked by oxygen atoms. In 1972 a new high-silica zeolite catalyst, HZSM-5, was discovered and has since been shown to have the ability to convert a remarkable range of materials to high-octane, aromatic, gasoline like products (Milne et al., 1990). This catalyst has been used for the conversion of vegetable oils to gasoline boiling range compounds. It has been reported that the activity and selectivity of these catalysts depend on factors such as acidity, pore size and distribution, and pore shape (Twaiq et al., 1999).

One of the first studies using the HZSM-5 catalyst to convert vegetable oils to hydrocarbons was conducted using corn and peanut oil (Weisz et al., 1979). The products were reported as percentages of fuel gas (C_1 and C_2 compounds), liquefied petroleum gas (C_3 and C_4 compounds), gasoline, and light distillate (jet fuel, kerosene, or light diesel and heating oils). A high degree of conversion to aromatics (benzene, toluene, and xylene) was found in all cases. The product mixture was found to be comparable to high grade gasoline and with an octane number of 90–96 showing the potential of this type of catalyst to produce a high quality, renewable motor vehicle fuel.

One group of researchers has extensively studied the conversion vegetable oils, primarily canola, over a variety of zeolite catalysts at a variety of reaction conditions (Katikaneni et al., 1995a,b,c, 1996; Prasad et al., 1986a,b) and with the addition of steam (Katikaneni et al., 1995a; Prasad et al., 1986a). The catalysts used include HZSM-5 as well as a variety of hybrids. Reactions were carried out in fixed bed micro reactors at temperatures between 300–500 °C, atmospheric pressure and WHSV (weight hourly space velocities) between 1.8–3.6 h^{-1}. Typical results showed high conversions (up to 100 wt.%) of the canola oil with high concentrations of aromatics in the organic liquid product fraction. It was also shown that the HZSM-5 catalyst was the most effective type of zeolite catalyst for converting vegetable oil to gasoline range hydrocarbons (Katikaneni et al., 1995a,b,c).

The pyrolysis of used sunflower oil in a fractionating packed column of varying lengths has been studied using the HZSM-5 catalyst (Dandik et al., 1998). The temperature ranged between 400–420 °C and the amount of HZSM-5 catalyst used was varied. Nearly complete conversion (96.6%) of the used oil and the maximum hydrocarbon yield (33%) was obtained at the highest temperature, catalyst content, and lowest column length. The liquid hydrocarbon phases consisted of *n*-alkanes, *n*-alkenes, and only small amounts of aromatics. These results are not typical of similar reactions but was attributed to the fractionating batch reactor configuration used. A significant percentage of gasoline boiling range hydrocarbons (C_5–C_{11}) was also produced.

Significant work has been done in Malaysia to convert palm oil into liquid hydrocarbons (Twaiq et al., 2003a,b, 2004; Sang et al., 2003, 2004) using mesoporous catalysts. In the first study by this research group, palm oil was cracked in a fixed bed microreactor at atmospheric pressure, temperatures ranging from 350–450 ° C and WHSV's between 1–4 h^{-1}. The catalysts used were HZSM-5, zeolite B, USY (Ultra-stable Y), hybrids of the three and HZSM-5 impregnated with potassium. The main findings were that the among the HZSM-5, Zeolite B and USY catalysts, the HZSM-5 had the highest conversion and gasoline yield, lowest coke formation, and had the highest selectivity for aromatics, however, it also had the highest yield of gaseous hydrocarbons. The potassium impregnated catalysts were shown to decrease the aromatic content of the gasoline product, likely due to a change in the acidity of the catalyst. The gasoline yield was shown to increase when the HZSM-5-USY hybrid catalyst was used.

The results of this study provided that basis for several follow-up studies by this research group. Although HZSM-5 catalysts are promising, they still exhibit high gas formation, which will decrease the formation of the desired liquid fraction. Different types of catalysts have been studied in attempt to minimize the gas fraction and maximize the liquid fraction. One option is mesoporous catalysts such as the MCM-41, which has shown to be selective for C_5 olefinic products (Twaiq et al., 2003a,b). The effect of pore size, surface area, and the percentage of alumina incorporated into the catalyst on the product distribution of cracked palm oil was studied (Twaiq et al., 2003a,b). It was found that an increase in alumina increased catalyst acidity and activity to an optimum level, however, the activity was lower than the HZSM-5 catalyst. Overall, the mesoporous catalysts resulted in lower gas formation but they were more selective for linear hydrocarbons in the diesel boiling range rather than gasoline range hydrocarbons (Twaiq et al., 2003a). It was also found that the surface area and pore size affected the selectivity for different product types. Both the HZSM-5 and MCM-41 catalysts show desirable characteristics for converting palm oil to liquid hydrocarbons. The synthesis of these two catalysts to create a composite zeolite-mesoporous catalyst was also studied (Twaiq et al., 2004). The results of this study showed that the composite catalysts showed good selectivity to the formation of aromatics. In a similar study the performance of HSZM-5, MCM-41 and the composite catalysts were compared (Sang et al., 2003). The composite catalyst resulted in the highest conversion (99 wt.%) and highest gasoline yield. Design of experiment (DOE) was also used to determine the effects of reaction variables and to optimize the reaction conditions for the production of aromatic gasoline fractions (Sang et al., 2004). Reaction temperature, catalyst ratio, and WHSV were found to be important operating variables in terms of the final product distribution. It was found the optimum yield of gasoline was found at a reaction temperature of 440 °C, fatty acid to catalyst ratio of 9.64, and WHSV of 3.66 h^{-1}.

The use of zeolite catalysts has shown to be effective at converting triglyceride based vegetable oils to liquid gasoline range hydrocarbons. These studies indicate that the nature of the catalyst significantly impacts the product distribution. It was recognized that although the HZSM-5 catalyst was shown to be highly effective, it still exhibited formation of gaseous products. In an attempt to minimize this fraction, mesoporous MCM-41 has been used. A hybrid of these two catalysts was found to be most effective at maximizing the gasoline fraction.

4.3. Transition metal catalysts

Transition metal catalysts have been used for the production of diesel like hydrocarbons from triglycerides (Craig, 1991; Craig and Coxworth, 1987; Craig and Soveran, 1993; da Rocha Filho et al., 1992, 1993; Gusmao et al., 1989; Monnier et al., 1998; Stumborg et al., 1996). These catalysts are traditionally used for hydroprocessing in the heavy oil industry at temperatures in the range of 350–450 °C with high hydrogen partial pressures (1–25 MPa). The formation of alkanes, alkylcycloalkanes and alkylbenzenes during the catalytic hydrocracking of vegetable oils was investigated by da Rocha Filho et al. (1992) using a $NiMo/Al_2O_3$ catalyst in the presence of elemental sulfur (da Rocha Filho et al., 1993). The vegetable oils tested included maracuja, tucuma, buriti, babassu, and soybean oils and the primary reaction products consisted of alkanes (65.3–76.8 wt.% of feed) primarily with carbon numbers ranging from C_{11}–C_{18}. Reactions were carried out in batch micro reactors at temperatures ranging from 350–450 °C and pressures between 7–14 MPa. In a similar study (da Rocha Filho et al., 1992) seringa and ucuuba oils were cracked using the same catalyst at 360 °C and 14 MPa (140 bar). Conversions of almost 100% were obtained and the primary products were found to be alkanes and cycloalkanes. The gas phase, aromatics, and acid values were not as significant. Vegetable oil cracking has also been studied in a batch reactor under high hydrogen partial pressure 1–20 MPa (10–200 bar) and at temperatures ranging from 350–400 °C. The corresponding products were essentially mixtures of *n*-alkanes.

Although vegetable oil fuel is considered an alternative source of energy, conventional refining technologies, already in place in the petroleum industry may be used to convert vegetable oils into hydrocarbons (Craig, 1991; Craig and Coxworth, 1987; Craig and Soveran, 1993; Stumborg et al., 1996). Craig and Coxworth (1987), used a conventional fluid catalytic cracking (FCC) bench scale unit and hydrocracking/hydrotreating techniques to convert canola oil into hydrocarbons. It was shown that the oil cracked readily and produced products with yields similar to conventional petroleum based feedstocks in the FCC unit and that subsequent hydrotreating yielded fuels in the diesel boiling range (Craig and Coxworth, 1987). In a similar study by the Saskatchewan Research Council (SRC), Natural Resources Canada, and Agriculture and Agri-Food Canada, a conventional medium severity hydroprocess was used to convert canola oil into a super cetane product in the diesel boiling range (Stumborg et al., 1996). The process consisted of a combination of hydrocracking, hydrotreating, and hydrogenation. These processes are described in greater detail in Canadian patent 1,313,200 (Craig and Soveran, 1993) and US patent 4,992,605 (Craig, 1991).

The success of these studies has led to the commercialization of a "super cetane" product to be used as a diesel fuel additive. This technology was developed by CANMET Technology Center, a division of Natural Resources Canada. This technology utilizes conventional refining technology with different fatty feeds. The product is separated into three fractions: naptha, middle distillates, and waxy residues. The middle distillate or super cetane has similar characteristics to diesel fuel and a cetane number of approximately 100. It is composed primarily of straight chain hydrocarbons (CANMET Energy Technology Center, 2004).

Tall oil is an alternative feed that can be used for the production of hydrocarbons using the aforementioned technologies. Tall oil has been subjected to similar hydrotreatments to produce diesel like fuel (Liu et al., 1998; Monnier et al., 1994, 1998). Tall oil differs in composition compared to other vegetable oil because it is composed of C_{18} fatty acids as well as other compounds such as resin acids, diterpenic hydrocarbons, and diterpenic alcohols and aldehydes (Feng et al., 1993). The resulting product is a high quality cetane enhancer that can be used as a fuel additive.

4.4. Sodium carbonate

Sodium carbonate catalyst has also been used in the pyrolysis of vegetable oils (Dandik and Aksoy, 1998b; Konwer et al., 1989; Zaher and Taman, 1993). Konwer et al. (1989) used solid sodium carbonate as a catalyst to produce liquid fuel from the pyrolysis of *Mesua ferrea* L. seed oil and the pure forms of its primary fatty acids including linolinic, linoleic, oleic, palmitic, and stearic acid. Earlier studies by this research group showed that pyrolysis of *M. ferrea* L. oil in the presence of 1% sodium carbonate and at 500 °C produced black pyrolytic oil similar to crude oil and that the fractions could be suitable for various applications including gasoline and diesel (Konwer et al., 1989). The unsaturated fatty acids produced significant concentrations of aromatics and lower concentrations of olefins, while the concentration of aromatics formed from the saturated fatty acids was very low and the olefin yield was high (Konwer et al., 1989). Analysis of the saturated components of the pyrolysis oil, which comprised 20–25 wt.% of both the saturated and unsaturated fatty acids, showed that the main products were *n*-alkanes. Sodium carbonate has also been used in pyrolysis of used sunflower oil in a reactor equipped with a fractionating packed column (Dandik and Aksoy, 1998b). Contrary to previous results (Konwer et al., 1989) this study showed very low concentrations of aromatics in the pyrolysis products. Conversions were lower than previous results (Konwer et al., 1989) and almost half of the feed formed coke-residual oil. The primary pyrolysis products consisted of liquid and gaseous hydrocarbons phases with lesser amounts of acids, water, H_2, CO, and CO_2. The liquid phase contained mostly C_5–C_{11} hydrocarbons (19.45–32.87%) and the gaseous phase was mainly composed of C_1–C_3 hydrocarbons (13.65–26.18%). Cottonseed oil was pyrolyzed in the presence of 1% sodium carbonate (Zaher and Taman, 1993). The thermally decomposed oil (approximately 70 wt.% of the original oil) was collected and analyzed. Alkanes were the primary products accounting for nearly 70% of the pyrolyzed oil. The products also contained 21.7% aromatics.

Dandik and Aksoy (1999) compared the pyrolysis of used sunflower oil using sodium carbonate, silica–alumina, and HZSM-5 catalysts. It was found that at the conditions tested, that the highest conversion (73.17 wt.%) was obtained using the sodium carbonate as a catalyst. The sodium carbonate also resulted in the highest yield of liquid product primarily consisting of gasoline range hydrocarbons.

A possible concern with sodium carbonate is that traces of sodium may be present in the product, impeding its use. In the literature reviewed, there were no reports of sodium present in the desired product, which was the organic oil. It is however, likely that the sodium carbonate first reacts with fatty acids to produce sodium salts which are then further decomposed into hydrocarbons as shown by results presented from Dandik and Aksoy (1998b) and Konwer et al. (1989).

4.5. Reaction mechanisms

4.5.1. Activated alumina catalysts

The mechanism for the deoxygenating of triglycerides to aliphatic hydrocarbons over activated alumina has been investigated (Vonghia et al., 1995). Unlike other catalysts, most notably zeolites, where determination of conversion pathways can be complex, activated alumina is ideal for studying primary decomposition pathways because it deoxygenates the substrate solely to acyclic alkenes and some alkanes (Vonghia et al., 1995). It was concluded that triglyceride decomposition occurs initially via two mechanisms, either a β-elimination to produce carboxylic acids or a γ-hydrogen transfer mechanism to yield alkenes as observed elsewhere (Bahadur et al., 1995), both occurring through a bonding of a carbonyl oxygen to a Lewis Acid site on the alumina catalyst. It is then postulated that the carboxylic acids form symmetrical ketones, which may undergo another γ-hydrogen transfer to produce monoalkenes and methyl ketones. The methyl ketones will eventually be converted to monoalkenes through an unknown mechanism followed by a dehydration or undergo the γ-hydrogen rearrangement. It is also believed that the methyl ketone can isomerizes into aldehydes, which are then oxidized to produce carboxylic acids. In order to better understand the cracking behavior and kinetics of catalytic conversion of triglycerides to hydrocarbons using an activated alumina catalyst, octanoic acid was used as a model compound in a series of cracking studies (Billaud et al., 2001, 2003). The results validated previous studies (Leung et al., 1995) and kinetic parameters were determined.

4.5.2. Molecular sieve catalysts

It has been reported that when using catalysts, the primary reaction step in the decomposition of a triglyceride is still the thermal breakdown of the triglyceride into heavy oxygenated components such as ketones and aldehydes (Katikaneni et al., 1996) as was postulated and verified

(1) Canola Oil $\rightarrow$ Heavy Oxygenated C_xH_y ***(thermal)***

(2) Heavy Oxygenated C_xH_y $\rightarrow$ Heavy C_xH_y + H_20 + CO_2 + CO ***(thermal and catalytic)***

(3) Heavy C_xH_y $\rightarrow$ Paraffins + Olefins (short and long chain) ***(thermal and catalytic)***

(4) Light Olefins $\rightleftarrows$ C_2-C_{10} Olefins ***(catalytic)***

(5) C_2-C_{10} Olefins $\rightleftarrows$ Aromatic C_xH_y + Aliphatic C_xH_y ***(catalytic)***

(6) Canola Oil $\rightarrow$ Coke ***(thermal)***

(7) *n*(Aromatic C_xH_y) $\rightarrow$ Coke ***(catalytic)***

Fig. 5. Proposed mechanism for the catalytic cracking of canola oil (Katikaneni et al., 1996).

earlier (Alencar et al., 1983; Chang and Wan, 1947; Idem et al., 1996; Schwab et al., 1988). A reaction scheme for the catalytic cracking of canola oil over zeolite type catalysts has been proposed and is shown in Fig. 5. After the thermal breakdown of the triglyceride molecule, the heavily oxygenated compounds are deoxygenated and then cracked into paraffins and olefins as a result of thermal and catalytic mechanisms (Fig. 5 – Eqs. (2) and (3)). The subsequent conversions of the light olefins into C_2–C_{10} olefins, aromatics and aliphatics (Fig. 5 – Eqs. (4) and (5)) are due to catalytic mechanisms such as cyclyzation and aromatization of C_2–C_{10} olefins in the pores of zeolites (Katikaneni et al., 1996). Coke is then produced thermally or catalytically by the polymerization of large aromatics (Katikaneni et al., 1996).

5. Properties of pyrolyzed triglycerides

Research on bio-diesel and its properties is very comprehensive; however, research on the properties of bio-oils from the pyrolysis of triglyceride materials such as vegetable oils and animal fats is not as common. There have been numerous studies conducted on pyrolysis of vegetable oils but few go into detailed characterization of the properties. Furthermore, the range of products produced in these studies varies considerably depending on the reactions conditions and whether or not a catalyst was used. In some studies the goal has been to produce gasoline range hydrocarbons and in others diesel range hydrocarbons. As well, some studies have separated the pyrolysis products by distillation and analyzed particular fractions.

5.1. Diesel

Diesel fuel ranks second in usage, behind only gasoline, as fuel for internal combustion engines (Hochhauser, 2004). Diesel fuel quality is assessed by measuring various properties related to handling and storage, safety, ignition and combustion, and engine performance (ASTM D 975-04c, 2005; Bahadur, 1994; Hochhauser, 2004). These tests are outlined in ASTM D975. Table 1 outlines some of the major requirements for No. 2 diesel fuel from both ASTM and EN standards. No. 2 diesel is the grade most commonly used for smaller trucks and automobiles.

The properties of the heavy fractions of pyrolysis oils from triglyceride materials both with and without catalysts have been investigated and compared to diesel fuel specifications (Agra et al., 1992; Boocock et al., 1992a,b; Niehaus et al., 1986; Schwab et al., 1988; Stumborg et al., 1996). These pyrolytic oils were produced by direct thermal cracking (Schwab et al., 1988; Lima et al., 2004; Niehaus et al., 1986), by hydroprocessing with transition metal type catalysts (Craig and Coxworth, 1987; Stumborg et al., 1996), and by catalytic pyrolysis with activated alumina (Boocock et al., 1992b), potassium hydroxide (Agra et al., 1992), with sodium carbonate (Zaher and Taman, 1993), and calcium oxide (Megahed et al., 2004).

Table 1
ASTM D 975 requirements for diesel fuel (ASTM D 975-04c, 2005)

Property	ASTM method	Grade no. 2-D S15
Flash point, °C, min	D 93	52
Water and sediment, vol.%, max	D 2709	0.05
Distillation temperature, °C, 90 vol.% recovered	D 86	
Min		282
Max		338
Kinematic viscosity, mm^2/s at 40 °C (104°F)	D 445	
Min		1.9
Max		4.1
Ramsbottom carbon residue on 10% distillation residue, mass%, max	D 524	0.35
Ash, mass%, max	D 482	0.01
Sulfur, mass%, max	D 129	–
	D 2622	0.05
Copper strip corrosion rating, max 3 h at 50 °C	D 130	No. 3
Cetane number, min	D 613	40
One of the following properties must be met		
(1) Cetane index, min	D 976–80	40
(2) Aromacity, vol.%, max	D 1319	35
Lubricity, HFRR @ 60 °C, micron, max	D 6079	520

The cetane number was determined for the pyrolysis products of soybean oil (Lima et al., 2004; Niehaus et al., 1986; Schwab et al., 1988), palm oil (Lima et al., 2004), and castor oil (Lima et al., 2004). The castor oil was the only oil whose pyrolysis products exhibited a lower cetane value than the specified ASTM value of 40. The cetane number is related to ignition delay or the amount of time it takes for combustion to begin after fuel injection. Short ignition delays correspond to high cetane numbers, which indicate good combustion and high fuel quality.

The viscosity of the pyrolytic oil has also been studied (Agra et al., 1992; Craig and Coxworth, 1987; Lima et al., 2004; Niehaus et al., 1986; Schwab et al., 1988; Stumborg et al., 1996). Viscosity, fuel's resistance to flow, is important in pump and fuel injector performance. If the viscosity of a fuel is too high, then the fuel will not atomize properly resulting in poor engine performance. Only two of the six studies that reported viscosity values (Niehaus et al., 1986; Schwab et al., 1988) found the viscosity to be higher than the specified value of 4.0 mm/s^2 (4.0 cSt), however in these cases the viscosity was measured at slightly lower temperature (37.8 °C) than the standard test method of 40 °C.

The cold flow properties of the pyrolytic oils have also been measured (Agra et al., 1992; Niehaus et al., 1986; Schwab et al., 1988; Stumborg et al., 1996). As in the case of bio-diesel, the cold flow properties of the pyrolysis oils are poor. The cold flow properties such as pour and cloud point measure the fuels ability to flow in cold temperatures by assessing the temperature at which long chain waxes or paraffins start to form. These highly viscous compounds may prevent proper flow of the fuel or plug filters. This property is especially important in climates with cold ambient temperatures. Typical cloud points range from 21–25 °C and pour points from 4.4–28 °C. These values are significantly higher than the cloud and pour points reported for No. 2 diesel (Graboski and McCormick, 1998).

Other properties have been measured including sulfur content (Lima et al., 2004; Niehaus et al., 1986; Schwab et al., 1988), specific gravity (Agra et al., 1992; Boocock et al., 1992a,b; Lima et al., 2004; Stumborg et al., 1996), ash content (Agra et al., 1992; Niehaus et al., 1986; Schwab et al., 1988; Stumborg et al., 1996), corrosion (Agra et al., 1992; Niehaus et al., 1986; Schwab et al., 1988; Stumborg et al., 1996), carbon residue (Agra et al., 1992; Schwab et al., 1988), and water and sediment (Schwab et al., 1988; Niehaus et al., 1986). The results show that these properties generally fall within the specified ranges for No. 2 diesel fuel regardless of whether or not a catalyst was used. Although lubricity of fuel is becoming a more important parameter, as shown by its addition to ASTM standards, none of these studies tested the lubricity of the pyrolyzed oil.

5.2. Gasoline

Gasoline is the most widely used motor vehicle fuel (Hochhauser, 2004). As with diesel, the quality of gasoline is also assessed by ASTM testing methods. The fuel quality of gasoline is measured by similar parameters to that of diesel fuels. The ignition quality of gasoline is measured primarily by its octane number also known as antiknock index (ASTM D 4814-04a, 2005). The octane number is calculated by taking the average of the research octane number and the motor octane number, which measure antiknock level under mild and more severe conditions, respectively.

Although many studies on producing hydrocarbons by vegetable oil pyrolysis report products in the gasoline range little work has been done testing the properties of the gasoline and comparing them to ASTM standards. In one study (Weisz et al., 1979) it was found that gasoline range hydrocarbons with octane numbers ranging from 90–96 could be obtained by catalytic conversion of the pyrolysis products of various vegetable oils.

6. Conclusions

Due to political, economic, and social factors there is a growing need for the development of renewable fuels and chemicals to supplement or supplant conventional petroleum derived products. Currently there are two processes which are at the forefront of biomass research. These include (1) pyrolysis of lignocelluslosic biomass to produce pyrolytic oils also known as bio-oil and (2) transesterification of triglycerides to produce bio-diesel. Research in the area of vegetable oil pyrolysis is not as abundant as research in other areas such as bio-oil and bio-diesel, but the studies to date indicate potential for production of non-oxygenated, liquid hydrocarbon mixtures. Possible applications include use as fuel or as feedstock in the chemical industry for the production of lubricants, solvents, or lacquers. The drawbacks associated with both the production and the final properties of bio-oils and bio-diesel has driven research in this area.

Due to these drawbacks, there is a need for the development of other alternative renewable or bio-based products. Ideally, these products would be more representative of petroleum products in both composition and properties, for example, non-oxygenated, stable, and with high heat contents. The pyrolysis of triglyceride materials to produce liquid hydrocarbon mixtures represents a process that has the potential to meet this need.

Pyrolysis of triglycerides can be divided into direct thermal cracking and catalytic cracking. Results of thermal cracking studies show that complex mixtures of products are produced. The difference in distribution of the final products between studies is heavily dependent on reaction variables such as the reactor type, residence time the composition of the initial feedstock, reaction temperature, as well as the collection procedure and analytical techniques used. The results of these studies provide general ideas as to what types of products may be achieved from this process. It is evident that liquid mixtures with high percentages of hydrocarbons can be obtained but in many of these studies undesirable, oxygenated compounds such as carboxylic acids and ketones still exist. The effect of reaction conditions on the final product distribution needs to be studied more extensively so that the reaction may be optimized to obtain the desired product. Areas where this research is lacking include optimization of the reaction conditions to obtain specific reaction products, understanding of the chemistry behind the pyrolysis reaction, and comprehensive evaluation of the final product properties.

The pyrolysis of vegetable oils in the presence of a catalyst is much more common than direct thermal cracking. The literature on catalytic cracking of vegetable oils can be grouped into four main catalyst types including (1) molecular sieve catalysts, (2) activated alumina catalysts, (3) transition metal catalysts and (4) sodium carbonate.

Hydroprocessing of vegetable oils using transition metal type catalysts is being produced commercially. The technology was developed by Natural Resources Canada and the resulting “super cetane” product can be used a diesel fuel additive and there are several patents in this area. This technology is attractive for areas where the hydroprocessing industry is well established; however, one of the main drawbacks is that it must be conducted under high pressure. These types of processes result in a diesel like products composed of linear hydrocarbons.

The use of molecular sieve type catalysts is very promising for the conversion of vegetable oils to highly aromatic gasolines. There have been numerous studies conducted utilizing a variety of different types of molecular sieve catalysts. The most popular catalyst is HZSM-5 catalyst and is has been shown that this catalysts is the more effective for converting various vegetable oils to gasoline type products than other zeolite hybrids. Research in this area is still largely being conducted at the lab scale. Now that is had been proven that these types of catalysts are effective for production of high quality gasolines research is shifting to optimization of the acidity, pore size, and configuration of the catalysts as well as the investigation of different families of molecular sieve catalysts.

Activated alumina and sodium carbonate catalysts have also shown to be effective at producing diesel type fuels however, studies are limited and there is room for more work in this area. They have not been studied as extensively as molecular sieve and transition metal catalysts, however both appear to be promising options. It has been shown that at high temperatures (450 °C) activated alumina has the ability to convert fatty acids and triglycerides into products with very little or no oxygen. This could be due to the nature of the catalyst which is effective at decarboxylation of fatty acids. Although there are few studies in this area, it appears that activated alumina is a promising catalyst for production of oxygen free pyrolytic oil.

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