

# Fluid Catalytic Cracking of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review

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**ABSTRACT:** To reduce the carbon footprint and greenhouse gas (GHG) emissions associated with heavy crude oil/bitumen upgrading and refining in the production of clean transportation fuels, researchers are targeting the production of fuels from renewable energy resources. These resources are mainly biomass-derived oils, which include oils produced by biomass pyrolysis (bio-oil), edible and inedible vegetable oils, and animal fats. Over the past 2 decades, research has focused on the evaluation of biomass-derived oil processing using conventional fluid catalytic cracking (FCC), a technology responsible for producing the majority of gasoline in a petroleum refinery. The present review summarizes research associated with the FCC of various biomass-derived oil feedstocks as well as studies related to the co-processing of these oils with conventional petroleum feedstocks. The objective of this review is to present a comprehensive perspective of the effects of renewable oil processing on existing FCC technology, operation, catalysts, and product quality and quantity.

## 1. INTRODUCTION

The limited availability of light and high-quality crude oils, increasing energy demand, and growing environmental concerns have made the use of oils from renewable sources an attractive option. Biofuel production from the processing of pure biomass-derived materials and the co-processing of these materials with petroleum-derived feedstocks have the potential to significantly reduce the carbon footprint [or greenhouse gas (GHG) emissions] all of the way through the processing chain of producing clean transportation fuels.

Co-processing of petroleum with feedstocks from renewable resources using existing refining catalysts, processes, and technologies offers advantages from both technological and economic perspectives. Because it utilizes the existing refining infrastructure and configuration, little additional capital investment is required. However, the refining of biomass-derived oils does present important challenges that need to be addressed, including their unique physical and chemical characteristics (high oxygen contents and highly paraffinic compositions), possible compatibility issues with petroleum feedstocks, effect of formed water on catalyst activity and stability, changes in reaction kinetics, mass and heat transfer, and the impacts of the final fuel products on engine performance and emissions.

Owing to the increasing demand for biofuels and the challenges that come with their production, a considerable amount of work has been published in the literature with respect to the processing of biomass-derived oils, particularly in the context of one of the most important technologies for fuel (mainly gasoline) production in a refinery, namely, fluid catalytic cracking (FCC). There have recently been published reviews by Butler et al.,<sup>1</sup> Bridgwater,<sup>2</sup> and Mortensen et al.<sup>3</sup> that have provided information related to the catalytic cracking of biomass-derived oils. This information, however, is limited to the cracking of pyrolysis oil (bio-oil) only. Butler et al.<sup>1</sup> provided a brief summary of recent laboratory research and commercial developments in bio-oil catalytic cracking. The review by Bridgwater<sup>2</sup> focused primarily on fast pyrolysis of biomass methods but included a list and brief descriptions of

various technologies available for further upgrading of the produced bio-oil. This author listed organizations that have been involved in catalytic cracking of bio-oils in the past decade. The review by Mortensen et al.<sup>3</sup> summarized bio-oil catalytic upgrading studies with a focus on reaction mechanisms, kinetic models, and catalyst deactivation.

It is important to note that, with regard to kinetic studies, only Adjaye and Bakhshi<sup>4,5</sup> established kinetic models to describe the catalytic conversion of bio-oils. These models were summarized by Mortensen et al.<sup>3</sup> The work by Ong and Bhatia<sup>6</sup> did include the proposal of a kinetic scheme for the catalytic cracking of a vegetable oil but did not provide any equations and kinetic parameters.

The objective of the present review is to evaluate and summarize the effects of renewable oil processing on existing FCC technology, operation, catalysts, and product quality and quantity. This review focuses on the processing of various pure renewable oils, including bio-oils derived from biomass pyrolysis, edible/inedible vegetable oils, and animal fats, as well as the co-processing of renewable oils with petroleum-derived feedstocks. It is organized and structured according to the type of biofeedstocks that have been studied in the literature. Under each biofeedstock, the work related to its processing (in its pure form) and its co-processing with conventional petroleum feedstocks is discussed.

## 2. BIOMASS-DERIVED FEEDSTOCKS

**2.1. Pyrolysis Oils (Bio-oils).** Pyrolysis of biomass leads to the production of bio-oil, a free-flowing liquid at room temperature. Bio-oil is typically dark brown in color, yet some can be black or green depending upon the chemical composition and the amount of microcarbon content.<sup>2</sup> Bio-oils have a high content of oxygenated compounds, which are foreign to petroleum refineries. Hence, while bio-oils can be potentially used as a renewable feedstock for the

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production of transportation fuels, such as gasoline and diesel, direct feeding of these oils into standard refinery units is challenging.<sup>7</sup> In addition to the significant amounts of oxygenated compounds that they contain, which include acids, aldehydes, ketones, alcohols, esters, ethers, glycols, and phenols,<sup>8</sup> bio-oils are highly viscous, corrosive, and relatively unstable materials that exhibit poor fuel properties<sup>9,10</sup> and low heating values.<sup>11–15</sup> These properties can be quite problematic with respect to FCC equipment, operations, catalysts, and the final product quality. Physical properties of bio-oils have been reviewed by Oasmaa and Peacocke<sup>16</sup> and Bridgwater,<sup>2</sup> while detailed chemical compositions have been assessed by Bertero et al.<sup>17</sup> Table 1 presents typical properties of bio-oils in comparison to conventional crude oil.

**Table 1. Comparison of Properties of Biomass-Derived Feedstocks to Conventional Crude Oil**<sup>3,18,19</sup>

property	bio-oil	crude oil
density at 15 °C (g/mL)	1.05–1.25	0.86–0.92
viscosity at 50 °C (cP)	40–100	180
water content (wt %)	15–30	<0.1
pH	2.8–3.8	N/A
heating value (MJ/kg)	16–19	44
C (wt %)	55–65	83–86
H (wt %)	5–7	11–14
O (wt %)	28–40	<1
S (wt %)	<0.05	<4
N (wt %)	<0.4	<1

Pyrolysis bio-oils have been investigated for catalytic cracking in a number of studies in the literature, which will be discussed in subsequent sections of this review. Studies involving the catalytic cracking of bio-oils are summarized in Table 2, and those involving the

**Table 2. Studies on the Processing of Pyrolysis Bio-oil via Catalytic Cracking**

feedstock	catalyst	reactor	reference
pyrolysis oil	HZSM-5, H–mordenite, H–Y, silicalite, silica–alumina	fixed-bed microreactor	4 and 43
pyrolysis oil	HZSM-5	fixed-bed microreactor	5 and 47
pyrolysis oil	HZSM-5	fixed-bed microreactor	20
pyrolysis oil	ZSM-5	fluidized bed	59
pyrolysis oil	HZSM-5	fixed-bed microreactor	23
pyrolysis oil	HZSM-5	fixed-bed microreactor	24
pyrolysis oil	La/HZSM-5	fixed bed	63

co-cracking of bio-oils with petroleum feedstocks are summarized in Table 3. The pyrolysis bio-oils that have been investigated in the context of FCC have come from various sources of biomass, such as Canadian oak,<sup>20</sup> pine wood,<sup>21,22</sup> aspen poplar wood,<sup>23</sup> maple wood,<sup>4</sup> and Swedish pine.<sup>24</sup>

**Table 3. Studies on the Co-processing of Pyrolysis Bio-oil with Petroleum Feedstocks via Catalytic Cracking**

feedstock		percent biomass in the feed mixture (wt %)	catalyst	reactor	reference
biomass component	petroleum component				
HDO	VGO	20	equilibrium catalyst (E-CAT)	fixed bed	22
HDO	long residue	20, 100	E-CAT	microactivity test (MAT) unit	64
flash pyrolysis liquid	LCO	15	ReUSY	MAT unit	58

**2.2. Vegetable Oils.** There is a substantial difference between the global consumption of petroleum [4.02 billion tons per year (BTY)] and the production of vegetable oils (0.12 BTY).<sup>25</sup> To meet anticipated legislative requirements in many developed countries for a 6–10% biofuel component in gasoline and diesel,<sup>26</sup> vegetable oils will have to be used in conjunction with fossil fuels and other renewable oils, such as pyrolysis bio-oils. Therefore, understanding the processing of vegetable oils and their blends with petroleum feedstocks in the context of FCC becomes important.

Several types of vegetable oils can be potentially used in the production of biofuels. Table 4 presents the various types of vegetable

**Table 4. Types of Vegetable Oils Used in FCC Studies**<sup>27–30</sup>

vegetable oil	main source	edibility
canola	Canada	yes
coconut	Philippines	yes
cottonseed	Greece/Turkey	no
palm	southeast Asia	yes
rapeseed	China/Europe	yes
soybean	U.S.A.	yes
sunflower	Europe	yes

oils that have been studied in the context of FCC and the principal geographical locations around the world where they are produced. These renewable potential feedstocks can be classified on the basis of whether they are suitable for human consumption (edible) or not (inedible). In addition to these vegetable oils, there are other less common oils that could be potential feedstocks for biodiesel production, including jatropha, karanja, linseed, rubber seed, mahua, neem, and castor oils. A complete list of edible and inedible vegetable oils as well as different types of animal fats that can be used as biofuel feedstocks can be found in ref 27.

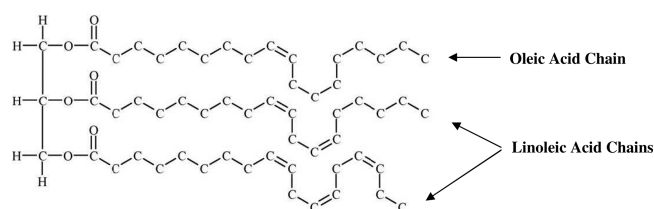
Vegetable oils exhibit differences in their saturated and unsaturated fatty acid compositions. Table 5 presents the typical compositions for

**Table 5. Typical Fatty Acid Composition of Vegetable Oils**<sup>32,33</sup>

	canola/rapeseed	cottonseed	palm	soybean	sunflower
unsaturated fatty acids	93	73	49	85	88
oleic acid (C18:1)	61	17	39	23	16
linoleic acid (C18:2)	21	55	10	54	71
$\alpha$ -linolenic acid (C18:3)	11	<1	<1	8	1
saturated fatty acids	7	27	51	15	12
palmitic acid (C16:0)	4	23	45	11	7
stearic acid (C18:0)	2	2	4	4	5
other	1	2	1	0	0

the vegetable oils used in FCC studies. It can be observed that these oils, with the exception of palm oil, consist predominantly of

unsaturated fatty acids, such as oleic and linoleic acids, the structures of which are presented in Figure 1. The presence of olefins in FCC



**Figure 1.** Molecular structure of a triglyceride molecule consisting of oleic and linoleic acid chains.<sup>34</sup>

feedstocks can significantly affect the product distribution, as these species are often involved in hydrogen-transfer reactions and other reactions that lead to the formation of aromatics.<sup>31</sup>

Several studies in the literature have been dedicated to investigate the catalytic cracking of different types of pure vegetable oils, including rapeseed, palm, soybean, cottonseed, and waste cooking oils. Other work has focused on the cracking of blends of petroleum feedstocks with these vegetable oils. These studies as well as those performed with animal fats and model compounds are summarized in Tables 6 and 7.

The catalytic cracking of rapeseed oil (RSO) or canola oil, which is a form of RSO having low levels of erucic acid in its oil and low levels of glucosinolates in its meal, has been investigated extensively. However, most studies examined RSO as a co-processing feed

**Table 6.** Studies on the Processing of Pure Vegetable Oils, Animals Fats, and Model Compounds via Catalytic Cracking

feedstock	catalyst	reactor	reference
Vegetable Oils			
rapeseed oil	E-CAT	MAT unit	75
rapeseed oil	E-CAT	plug-flow micriser	34
rapeseed oil	NaY, clinoptilolite, HZSM-5, HY, $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	batch	84 and 104
palm oil	E-CAT	MAT unit	75
palm oil	nanozeolite beta	fixed bed	79
palm oil	carbon, MgO/carbon	batch	44
soybean oil	E-CAT	MAT unit	75
soybean oil	NaY, clinoptilolite, HZSM-5	batch	104
cottonseed oil	E-CAT	fixed fluidized bed	60
sunflower oil	NaY, clinoptilolite, HZSM-5	batch	104
ginger oil	MFI, BEA, FAU	fixed bed	85
waste cooking oil	NaY, clinoptilolite, HZSM-5	batch	104
waste cooking oil	nanozeolites (ZSM-5, Y, beta)	fixed bed	109
vegetable oil sludge	ZSM-5/MCM-41	MAT unit	110
Animal Fat			
chicken fat	USY/ZSM-5	two-stage fluidized bed	37
Model Compounds			
glycerol, sorbitol	E-CAT, Al <sub>2</sub> O <sub>3</sub> , USY zeolite, ZSM-5, SiC	MAT unit	40
ketones, acids, alcohols, aldehydes	HZSM-5	fixed bed	117
phenols	ZSM-5	tubular	115
alcohols, phenols	HZSM-5	fixed bed	57
ketones	HZSM-5	fixed bed	118

component during FCC. The catalytic cracking of pure palm oil has been studied by several groups, although, in comparison to the co-processing of rapeseed oil or bio-oil with petroleum fractions, the co-processing of palm oil is much less studied and the number of published papers is very limited. Other types of vegetable oils that have been investigated to some degree include soybean oil (SBO) and cottonseed oil (CSO). Although the use of waste cooking oil (WCO) has a number of advantages from an environmental perspective, catalytic cracking of WCO has also been explored minimally in published studies.

**2.3. Animal Fats.** Animal fats have not been examined as extensively as bio-oils and vegetable oils as potential feedstocks for FCC, as observed in Tables 6 and 7. These fats are usually obtained as byproducts from meat rendering and processing. Of animal-sourced substances, chicken fat contains a high level of linoleic acid, ranging between 17.9 and 22.8%.<sup>35</sup> Beef tallow, on the other hand, contains a significant amount of oleic acid (between 47 and 50%) and also has a moderate combination of saturated fatty acids (~40%), namely, palmitic and stearic acids.<sup>36</sup>

The processing of animal fats for the production of high-quality biofuels has been investigated by a few research groups. Two of the more significant works are by Tian et al.<sup>37</sup> and Melero et al.<sup>38</sup>

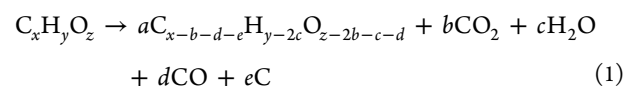
### 3. CHEMISTRY

The FCC process is very important to modern day refineries because of its flexibility to adapt to changing feedstock and product demand.<sup>22</sup> The chemistry significantly depends upon the type of feedstock, reaction conditions, and catalysts used in the process.

Catalytic cracking chemistry of biomass-derived oils involves conventional FCC reactions, such as protolytic cracking (cleavage of carbon–carbon bonds), hydrogen transfer, and isomerization,<sup>39</sup> as well as deoxygenation reactions, such as dehydration, decarboxylation, and decarbonylation.<sup>3</sup> Figure 2 illustrates reactions associated with the catalytic conversion of biomass-derived oils. It is important to note that deoxygenation of these biofeedstocks is essential because oxygen must be removed and replaced by hydrogen to produce liquid fuels.<sup>40</sup> Typical FCC catalysts, which consist of a mixture of an inert matrix, an active matrix, a binder, and a Y-zeolite, are efficient in removing oxygen from biomass-derived molecules.<sup>22,41</sup>

Dehydration reactions occur on the catalyst acid sites during the catalytic cracking of oxygenated compounds. This leads to the formation of water and a dehydrated compound, which may include ketones (Figure 2), aldehydes, and alcohols. Decarboxylation and decarbonylation reactions result in the formation of CO<sub>2</sub> and CO, respectively, as illustrated in Figure 2. The generation of these gases may pose concerns for refiners because they are not typical products of conventional petroleum catalytic cracking.

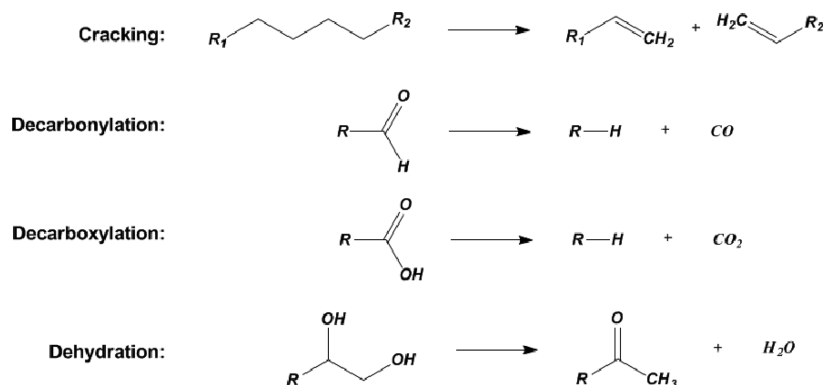
A simplified reaction pathway of the removal of oxygen to form CO, CO<sub>2</sub>, or water was proposed by Fogassy et al.<sup>22</sup>



Corma et al.<sup>40</sup> proposed mechanisms for the catalytic cracking of bio-oils to describe two categories of reactions, one that results in the generation of hydrogen and the other that leads to the consumption of hydrogen. In the former, hydrogen can be produced through steam-reforming reactions, dehydrogenation of carbohydrates and hydrocarbons, water–gas shift reactions, and decarbonylation, as shown in Figure 3. The hydrogen produced in these reactions is often consumed during hydrogen transfer, a bimolecular reaction involving two molecules that

**Table 7. Studies on the Co-processing of Vegetable Oils, Animal Fats, and Model Compounds with Petroleum Feedstocks via Catalytic Cracking**

feedstock		percent biomass in the feed mixture	catalyst	reactor	reference
biomass component	petroleum component				
Vegetable Oils					
rapeseed oil	VGO–residue blend	7.5, 15 vol %	E-CAT	continuous FCC pilot plant	75
rapeseed oil	hydrowax	20, 40 wt %	E-CAT, E-CAT/ZSM-5	microriser reactor	34
rapeseed oil	VGO	20–100 mol %	ReUSY/ZSM-5	continuous FCC pilot plant	102
rapeseed oil	VGO	20–100 wt %	E-CAT	continuous FCC pilot plant	88
palm oil	VGO	0, 30, 100 wt %	E-CAT	MAT unit	38
palm oil	VGO	50 wt %	USY/ZSM-5	two-stage riser FCC unit	37
palm oil		20–100 wt %	E-CAT	continuous FCC pilot plant	88
soybean oil	VGO	0, 30, 100 wt %	E-CAT	MAT unit	38
soybean oil		20–100 wt %	E-CAT	continuous FCC pilot plant	88
waste cooking oil	VGO	0, 30, 100 wt %	E-CAT	MAT unit	38
Animal Fat					
inedible animal fat (grease)	VGO	0, 30, 100 wt %	E-CAT	MAT unit	38
chicken fat	VGO	50 wt %	USY/ZSM-5	two-stage riser FCC unit	37
Model Compounds					
phenol, acid, ketone	gas oil	6–10 vol %	E-CAT/ZSM-5	advanced cracking evaluation (ACE) unit	119
glycerol	VGO	10–33 vol %	fresh USY zeolite	MAT unit	40
phenols	<i>n</i> -heptane	1.2 wt %	HMF1	fixed bed	103
phenol	gas oil	1.2, 4.0 wt %	E-CAT, HZSM-5	ACE unit	116

**Figure 2.** Reactions during the catalytic conversion of biomass-derived feedstocks.

leads to the formation of alkanes, as shown in Figure 4.<sup>42</sup> The resulting hydrocarbons will then undergo traditional oligomerization cracking chemistry of hydrocarbons.<sup>40</sup>

Adjaye and Bakhshi<sup>43</sup> also proposed a reaction network for the catalytic cracking of pyrolysis bio-oils, as presented in Figure 5. Unlike petroleum feedstocks and other renewable feedstocks, such as vegetable oils and animal fats, the cracking of bio-oils using acidic zeolites can produce challenging and undesirable products, such as tar and/or char. The effects of these byproducts are discussed in the subsequent catalytic cracking section of this review. Figure 5 also shows that oxygenated compounds in bio-oils can be converted to water, CO, and CO<sub>2</sub>.

Reaction mechanisms for the catalytic cracking of triglyceride molecules in vegetable oils were described by Tani et al.<sup>44</sup> Triglycerides are first hydrolyzed to glycerine and three fatty acid molecules, which include saturated and unsaturated types, as illustrated in Figure 6. This step is followed by dehydration of the glycerine to form water and gaseous hydrocarbons, as

shown in Figure 7. As for the fatty acids, they can undergo either decarbonylation/dehydration reactions to form CO and water or decarboxylation to produce CO<sub>2</sub> and hydrocarbons, which include paraffins and olefins, as shown in Figure 8. According to Dupain et al.,<sup>34</sup> dehydration reactions are more significant than the others. Tani et al.,<sup>44</sup> however, observed decarboxylation to be the predominant reaction. The reason for the discrepancy could be due to the fact that Tani et al.<sup>44</sup> used an agitated flow system with longer reaction times (in the order of hours) and MgO catalysts, which could promote decarboxylation and water–gas shift reactions, whereas Dupain et al.<sup>34</sup> used conventional FCC catalysts and a microriser reactor with more realistic FCC reaction times (in the order of seconds). Bulushev and Ross<sup>45</sup> proposed two reaction pathways for the conversion of fatty acids present in biomass-derived feedstocks to hydrocarbons: decarboxylation (eq 2) and decarboxylative ketonization (eq 3), which take place at temperatures lower than 400 °C. The latter is not common

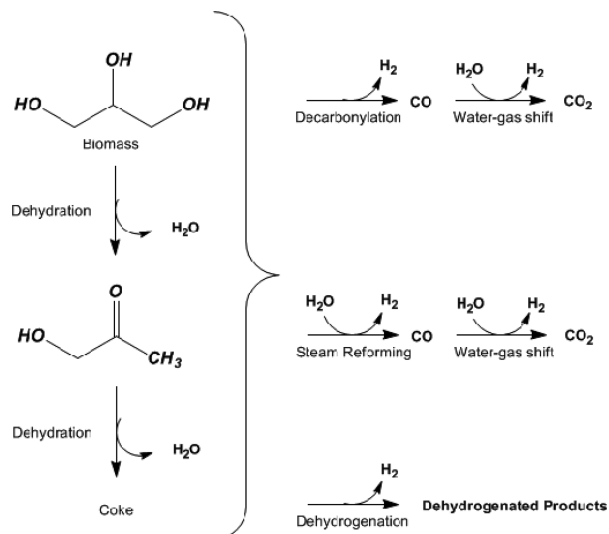
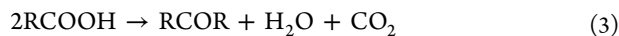


Figure 3. Hydrogen-producing reactions during the catalytic cracking of bio-oil.<sup>40</sup>

in FCC because reaction temperatures are typically above 500 °C.



The paraffin and olefin hydrocarbons produced from decarboxylation of fatty acids can range from C<sub>10</sub> to C<sub>18</sub>, depending upon the type of fatty acid from which they are derived. This depends upon the type of vegetable oil used as the feedstock. The hydrocarbon compounds can then undergo traditional FCC chemistry, which include cracking, isomerization, and hydrogen transfer. Leng et al.<sup>46</sup> proposed a more detailed reaction network associated with vegetable oil cracking that includes the types of hydrocarbons generated in the process, as presented in Figure 9.

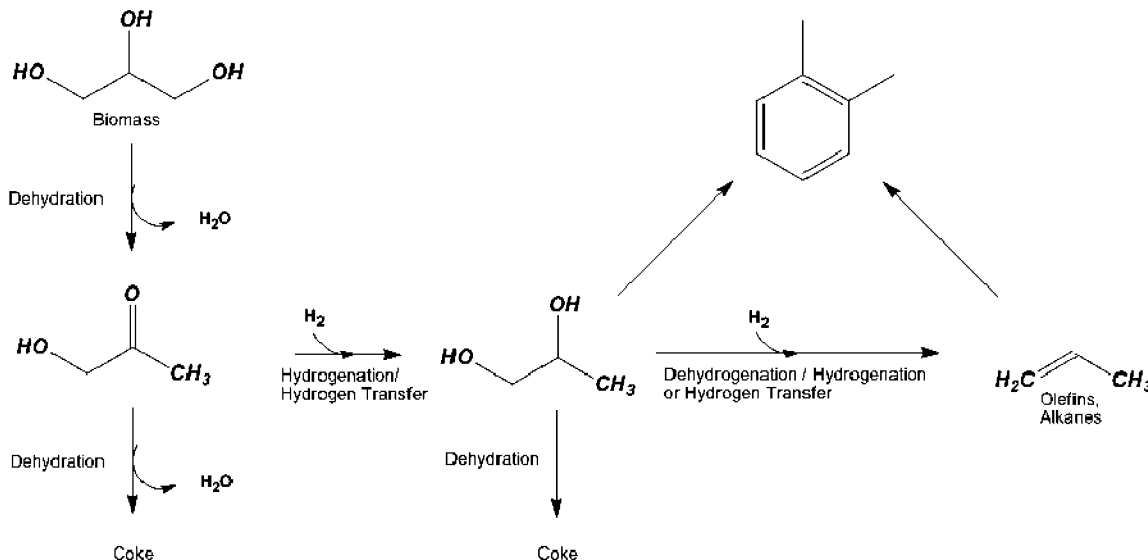


Figure 4. Hydrogen-consuming reactions during the catalytic cracking of bio-oil.<sup>40</sup>

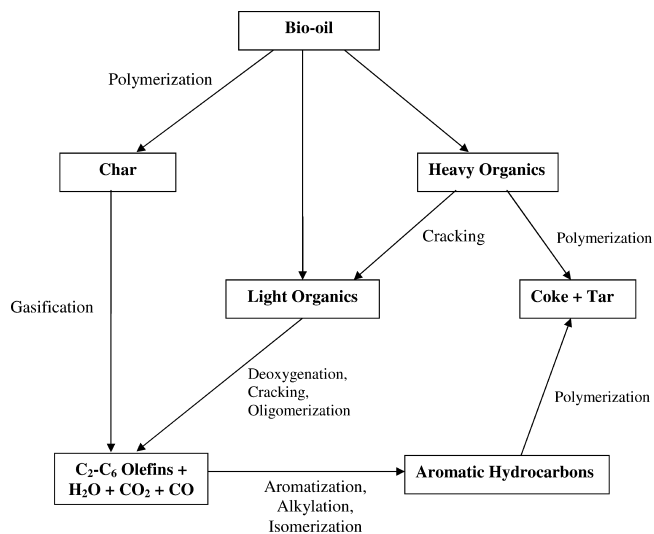


Figure 5. Proposed reaction pathway in the catalytic cracking of bio-oil over acidic zeolite catalysts.<sup>43</sup>

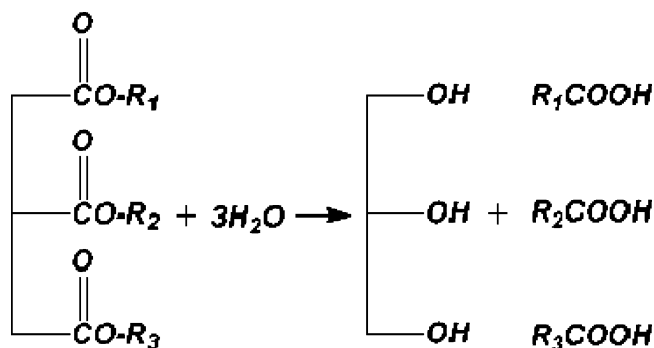


Figure 6. Reaction mechanism for the catalytic cracking of triglycerides.

#### 4. CATALYTIC CRACKING

The following subsections summarize the results and observations reported in published studies on processing

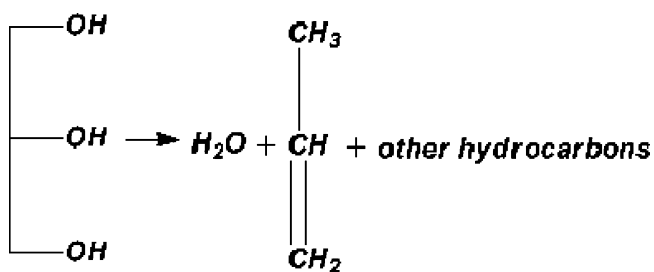


Figure 7. Water and gaseous hydrocarbons from the dehydration of glycerine.<sup>44</sup>

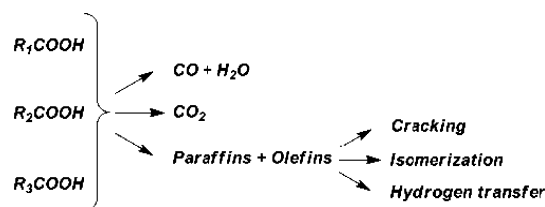


Figure 8. Conversion of fatty acids during FCC.

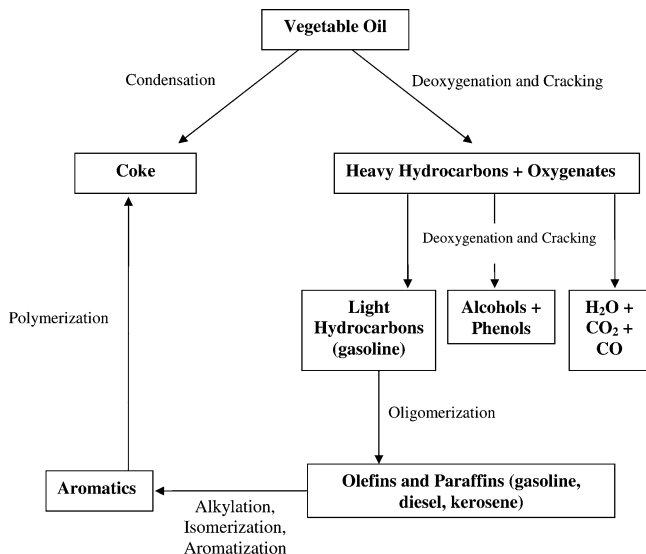


Figure 9. Reaction pathways during the catalytic cracking of vegetable oils.<sup>46</sup>

biomass-derived oils and co-processing these oils with conventional petroleum-derived feedstocks using FCC technology.

**4.1. Pure Pyrolysis Bio-oils.** As previously mentioned, pyrolysis bio-oils from various wood sources have been studied extensively as potential feedstocks for catalytic cracking. This section reviews the results of converting these bio-oils using various process conditions and catalysts and their effects on the FCC process.

**4.1.1. Product Distribution.** Upgrading of pyrolysis bio-oils via FCC leads to the formation of a wide range of products. The main products of catalytic conversion of these oils using conventional HZSM-5 and H-Y zeolites include a liquid oil product, water, coke, char, tar, and gases (predominantly  $\text{CO}_2$ , some hydrocarbons, and  $\text{CO}$ ).<sup>24</sup>

As with other technologies, product distributions are highly dependent upon operating conditions and catalyst type. For instance, it has been shown by Adjaye and Bakhshi<sup>47</sup> that, at temperatures above  $300\text{ }^\circ\text{C}$  and with the HZSM-5 catalyst, the

distillate product consisted of two fractions, an organic phase and an aqueous phase. However, at lower temperatures ( $<300\text{ }^\circ\text{C}$ ), a single homogeneous distillate fraction was obtained.

Horne and Williams<sup>21</sup> found that lower than desirable amounts of gasoline and total hydrocarbon products were obtained using ZSM-5 zeolites in a fluidized-bed reactor at cracking temperatures below  $500\text{ }^\circ\text{C}$ . These authors observed that higher temperatures ( $500\text{--}550\text{ }^\circ\text{C}$ ) were necessary to maximize the total hydrocarbon product yield. However, operating at such conditions led to an increase in the formation of gaseous products at the expense of liquid hydrocarbons.<sup>21</sup> Diebold and Scahill<sup>48</sup> and Evans and Milne<sup>49</sup> reported a maximum of 18 wt % total hydrocarbons produced using HZSM-5 at temperatures above  $400\text{ }^\circ\text{C}$ . A similar low yield of the total hydrocarbon product was obtained during the catalytic upgrading of pyrolysis vapors using ZSM-5 at  $500\text{ }^\circ\text{C}$ .<sup>50,51</sup> However, while some studies recommend reaction temperatures above  $500\text{ }^\circ\text{C}$  to optimize the liquid oil yield, Adjaye and Bakhshi<sup>47</sup> suggested that the maximum distillate yield could be obtained at  $370\text{ }^\circ\text{C}$  with a ZSM-5 zeolite in a fixed-bed microreactor. At higher temperatures, a decrease in the liquid product yield occurs because of the conversion of bio-oil to both gaseous and coke products. This is because, at elevated temperatures, secondary cracking and aromatization/polymerization reactions are favored. Similar results were obtained by Sharma and Bakhshi<sup>52</sup> with HZSM-5. It is important to note that coking with bio-oil is more severe than with heavy oils and oil sand-derived feedstocks, which normally do not have coking problems below  $400\text{ }^\circ\text{C}$ .<sup>47</sup> Vitolo et al.<sup>24</sup> suggested  $450\text{ }^\circ\text{C}$  as the optimal temperature to maximize the conversion of raw bio-oil to upgraded oil using HZSM-5 catalysts because, at this temperature, the yields of char and coke were minimal compared to those at other temperatures (between  $410$  and  $490\text{ }^\circ\text{C}$ ). However, there are advantages associated with higher operating temperatures, which include reductions in the aqueous fraction yield and in tar formation because of a higher gasification rate.<sup>21</sup>

Besides temperature, reaction time also has a substantial effect on the product distribution. Reduction in reaction time results in an increase in the oil fraction yield and a decrease in the yields of gas, coke, and char as observed by Adjaye and Bakhshi<sup>47</sup> using ZSM-5. Reduced coke formation is due to fewer condensation/polymerization reactions that take place inside the catalyst bed, since there is not enough time to convert bio-oil compounds into the heaviest and final products of the thermochemical treatment.<sup>47</sup> While decreasing the residence time seems to have clear advantages, especially with respect to diminishing catalyst deactivation by coke, one obvious disadvantage is that the degree of deoxygenation of the oil will also be reduced.

Aside from varying FCC process conditions, it has been shown that the use of steam during catalytic processing can also enhance distillate production. In addition to the greater amount of the distillate fraction produced, a significant reduction in coke formation was observed by Adjaye and Bakhshi<sup>4</sup> using HZSM-5, which was attributed to the promoted adsorption processes, cracking, deoxygenation, and aromatization reactions in the presence of steam.

With regard to char, it has been reported that a significant amount of this solid carbonaceous material is produced at lower reaction temperatures. In fact, it was observed in several studies that the formation of char took place mainly above the catalyst bed on the inner walls of the reactor.<sup>24,47</sup> This may be

attributed to the lower degree of volatilization of the bio-oil before it contacts the catalyst bed in the reactor. As the liquid bio-oil feed is injected into the reactor, it undergoes rapid heating before contacting the catalyst, which causes the separation of the bio-oil components into light organics, heavy organics, and char, with the latter being formed by polymerization of some unstable components in the raw bio-oil.<sup>24</sup> This thermal effect represents a major issue in bio-oil upgrading using liquid feeds.

In comparison to gasoline produced from petroleum-derived gas oil feedstocks, biogasoline derived from pyrolysis bio-oil had a higher aromatic content, as reported by Guo et al.,<sup>53,54</sup> who studied catalytic cracking of bio-oil using HZSM-5 zeolites in a fixed-bed reactor. This is expected as a result of the lack of available hydrogen in the catalytic cracking environment, since no hydrogen is provided externally in FCC. The main aromatic compounds found in the gasoline fraction included toluene, ethylbenzene, xylene, and trimethylbenzenes.<sup>53,54</sup> The amount of benzene produced, on the other hand, was negligible as a result of the alkylation that benzene molecules frequently undergo on acidic zeolite catalysts.<sup>55,56</sup> Other compounds found in the gasoline fraction produced depend upon the cracking temperatures. For instance, it was observed by Adjaye and Bakhshi<sup>47</sup> that ketones, phenols, ethers, and esters were present in the distillates stream when bio-oil was catalytically cracked at temperatures ranging between 290 and 300 °C. As the reaction temperature was increased to 370 °C and above, the distillates contained mostly aromatics and only a small amount of phenols and ketones. The absence of most oxygenated compounds at higher temperatures indicates the effectiveness of the HZSM-5 catalyst, which is able to convert these oxygenated compounds to hydrocarbons. Similar results were obtained when the space velocity was reduced.<sup>52</sup>

Some researchers have conducted studies to upgrade the aqueous fraction of biomass pyrolysis oils. Gayubo et al.,<sup>57</sup> for example, studied catalytic conversion of the aqueous fraction obtained at 450 °C using the HZSM-5 catalyst. The main non-oxygenated products were propylene, aromatics, butenes, ethylene, C<sub>5</sub>+ olefins, and C<sub>4</sub>+ paraffins. It was found that an increase in time-on-stream caused a reduction in catalyst activity because of coke deposition as well as an increase/decrease in the concentrations of oxygenated/non-oxygenated compounds, respectively.

**4.1.2. Coking.** Most published studies of catalytic cracking of pure bio-oil have reported irreversible deactivation of the catalyst mainly because of the high oxygen content in the feed.<sup>24,47,58,59</sup> This rapid deactivation was also reported when biomass-derived pyrolytic vapors were upgraded in a fixed bed using ZSM-5 catalysts,<sup>48</sup> with coke content accounting for over 50 wt % in the products.<sup>21,50,51</sup> Guo et al.<sup>53,54</sup> also observed coke yields of over 30 wt % during cracking bio-oil using HZSM-5 zeolite. Even when bio-oil was processed at low reaction temperatures (~400 °C), the coke yield tended to remain significant, reaching about 12 wt %, as reported by Adjaye and Bakhshi.<sup>4</sup> While coke is the main cause of reversible catalyst deactivation, it does not significantly contribute to irreversible deactivation. Causes for the latter, which have not been adequately studied in the literature especially in the context of bio-oils, have been suggested by Li et al.<sup>60</sup> in their cottonseed oil catalytic cracking work. These researchers attributed the irreversible catalyst deactivation to the presence of steam at high regeneration temperature, as steam led to the dealumination of zeolites.

**4.1.3. Catalysts.** Catalyst selection is important in bio-oil upgrading because the conversion of bio-oil and product distribution are highly dependent upon the type of catalyst used. As previously mentioned, the two most commonly used and effective zeolite catalysts in FCC processes are H-Y zeolites and HZSM-5. A study by Adjaye and Bakhshi<sup>43</sup> compared various catalysts during the catalytic conversion of biomass-derived pyrolysis oils, which includes the two aforementioned catalysts as well as H-mordenite, silicate, and silica-alumina catalysts. It was found that HZSM-5 was the most effective catalyst to upgrade pyrolysis oil for the production of organic distillates, overall hydrocarbons, and aromatics. HZSM-5 also yielded the least amount of coke, which can be attributed to its high acidity as verified by Vitolo et al.<sup>20,24</sup> It was also found that the silica-alumina catalyst was the most effective for minimizing char formation.

There is some discrepancy in the literature with respect to the role of H-Y zeolites during bio-oil catalytic cracking. Adjaye and Bakhshi<sup>43</sup> concluded that these zeolites are the most effective for minimizing tar formation and maximizing the production of aliphatics, whereas Vitolo et al.<sup>20</sup> reported high tar, char, and coke yields with a similar catalyst. The latter research group attributed their results to the small pore sizes in H-Y zeolites, which limit the maximal dimension of the products formed and, hence, led to shape-selective coke formation reactions.<sup>61,62</sup> It should be noted that long reaction times were used in the experiments conducted by Adjaye and Bakhshi<sup>43</sup> and Vitolo et al.,<sup>20</sup> which are not representative of commercial FCC operation. With regard to tar, it is generally accepted that acidic zeolites are better at reducing tar compared to less acidic silica-alumina and non-acidic silicalite catalysts.<sup>43</sup> At FCC reaction temperatures above 450 °C, dealumination of zeolites becomes quite significant, with this dealumination being the result of the high water content in the reaction medium. Dealumination causes irreversible deterioration of the total acidity, although the acid strength of the remaining sites is hardly modified.<sup>57</sup>

Gong et al.<sup>63</sup> assessed the catalytic cracking of bio-oil using various loadings of lanthanum (La) in a HZSM-5 catalyst in a fixed-bed reactor at 550–650 °C to maximize the production of light (C<sub>2</sub>–C<sub>4</sub>) olefins. While varying the amount of La added to HZSM-5 zeolite from 0 to 7 wt % did not influence the bio-oil conversion or the selectivity of CO and CO<sub>2</sub>, it did affect the selectivity of light olefins. The selectivity to the light olefins was increased to 60 mol % at 550 °C when 7 wt % La was added. As the loading of La exceeded 10 wt %, a decrease in bio-oil conversion and light olefin yield was observed.

**4.1.4. Effect on Process.** Pyrolysis bio-oils have been shown to present major problems during FCC operation. These problems are mainly related to reactor plugging<sup>58</sup> as a result of the formation of significant amounts of coke, tar, and char.<sup>24,59</sup> The formation of char is a result of the polymerization of unstable components present in bio-oils,<sup>24</sup> including aromatic hydrocarbons and phenols.<sup>47</sup> Residue formation was also reported because of polymerization/condensation reactions of oxygenated compounds in bio-oils, mainly ether species.<sup>47</sup> Figure 5 shows how char, tar, and coke products are formed within the reaction network of bio-oil catalytic conversion, as proposed by Adjaye and Bakhshi.<sup>43</sup>

**4.1.5. Summary.** (1) Product yields and distributions obtained from the catalytic cracking of pyrolysis bio-oils are highly dependent upon operating conditions and catalyst type. (2) Biogasoline derived from pyrolysis bio-oil has higher

aromatic content than conventional gasoline. (3) Char and coke formation is substantial, even at lower reaction temperatures. These have been found to cause significant reactor plugging issues. (4) Bio-oil cracking leads to irreversible catalyst deactivation (dealumination) mainly because of the high oxygen content in the feed and, consequently, high water/steam content in the reaction medium. (5) HZSM-5 is an effective catalyst to upgrade pyrolysis oil for the production of organic distillates, overall hydrocarbons, and aromatics. HZSM-5 also yields less coke than other zeolites because of its high acidity.

**4.2. Co-processing of Bio-oil with Petroleum Feedstocks.** While the catalytic cracking of pure bio-oils in a FCC unit presents major challenges, as discussed in the previous section, co-processing such feedstocks with conventional petroleum-derived feedstocks might be a more practical option. However, prior to co-cracking bio-oils with petroleum feeds, they must undergo hydrotreatment to reduce the high concentrations of heteroatoms (i.e., oxygen) to avoid rapid FCC catalyst deactivation. Hence, most published studies have investigated the co-processing of hydrotreated biomass-derived pyrolysis oils with conventional FCC feedstocks, namely, vacuum gas oil (VGO) or light cycle oil (LCO), to assess the suitability of using hydrodeoxygenated bio-oils (HDO oils) as potential FCC feedstocks. Moreover, it has been reported that catalytic cracking of HDO oils is more practical for those produced at more severe hydroprocessing conditions. The more the HDO oil is upgraded, the lower the coke and dry gas yields obtained during FCC.<sup>64</sup> However, if co-fed with conventional VGO feedstocks in sufficient quantities, bio-oils do not require complete hydrodeoxygenation to eliminate the highly reactive functional groups that lead to catalyst deactivation and unsuccessful FCC co-processing.<sup>64</sup> In such cases, HDO can be performed at lower temperatures and with less hydrogen.

**4.2.1. Conversion.** The overall conversion obtained during the co-processing of HDO oil and petroleum-based feedstocks depends upon the type of the latter. For instance, Fogassy et al.,<sup>22</sup> who used a fixed-bed reactor and a FCC equilibrium catalyst containing about 15 wt % Y zeolite, noticed that higher conversions were attained during HDO oil/VGO mixture experiments versus those obtained using a pure VGO feed, especially at catalyst/oil ratios below 5. At higher catalyst/oil ratios, the conversions obtained with the mixture and the pure VGO feeds were fairly similar. However, the opposite effect was observed when a bio-oil was co-processed with heavier petroleum-based feed, such as vacuum residue. A study involving the use of a petroleum feedstock with a final boiling point of 585 °C was performed by de Miguel Mercader et al.<sup>64</sup> using a commercial equilibrium catalyst (E-CAT). These authors observed that slightly higher catalyst/oil ratios were required to co-process HDO oil with the residue to obtain equivalent conversions to those attained with the pure residue feed. In other words, using the same catalyst/oil ratios for the mixture feed as those for the pure residue feed would result in lower conversions. It would be difficult to attribute the differences in the trends obtained from each study to the type of the catalysts being used, because the properties of the equilibrium catalysts used in both studies were not specified. Another study on the co-cracking of a hydrotreated biomass flash pyrolysis liquid with LCO using various catalysts showed that the conversion of this mixture was always lower than that of the ordinary VGO, which ranged between 60 and 80 wt %.<sup>58</sup>

Thus, it can be generally concluded that the conversion of nonconventional feedstocks is a complicated function of their reactivity, interaction with petroleum-based compounds, and process conditions.

It is expected that increasing the temperature results in higher conversion of HDO oil/VGO feed mixtures. Indeed, Samolada et al.<sup>58</sup> observed an increase in conversion of bio-oil/LCO mixtures from 18 to 32 wt %, when the temperature was raised from 500 to 550 °C in a microactivity test (MAT) fixed-bed unit. However, they indicated that performing cracking at even higher temperatures should be avoided to prevent secondary reactions that would lead to additional gas and coke formation.

**4.2.2. Product Properties.** Co-processing bio-oils with conventional FCC feedstocks provides several disadvantages with respect to fuel product properties. It was reported by Ikura et al.<sup>65</sup> that, as the concentration of HDO oil blended in diesel increased, the cetane number decreased. Moreover, the corrosivity of a HDO oil/diesel mixture was higher than that of pure petroleum diesel, and the viscosity of the mixture increased as the fraction of HDO oil increased.<sup>66</sup> However, blending HDO oil with petroleum fractions lowered the micro carbon residue (MCR) content.<sup>64</sup> A low MCR content in the blend is usually an important prerequisite for co-processing but does not guarantee a desirable product yield structure. Other advantages of co-processing include an increase in the hydrogen/carbon ratio (H/C) and a reduction in reactivity of oxygenated compounds, such as ketones and aldehydes.<sup>64</sup>

**4.2.3. Product Distribution.** Differences in the product distributions obtained from the catalytic cracking of bio-oil/petroleum mixtures versus pure petroleum feeds are apparent. For example, bio-oil/VGO mixture feeds cracked in a fixed-bed reactor using an industrial FCC catalyst containing 15 wt % Y zeolite by Fogassy et al.<sup>22</sup> provided higher low-value dry gas (H<sub>2</sub>, CO, CO<sub>2</sub>, and C<sub>1</sub>–C<sub>2</sub>) yields than a pure VGO feed, with ethylene making up nearly 50% of the dry gas fraction and the CO concentration being very low. This finding was attributed to the more extensive thermal cracking of HDO oil and the decomposition of oxygenates in the feeds. It was also reported that the yields of gaseous hydrocarbon compounds obtained during co-processing increased rapidly with conversion.<sup>22</sup> Despite the greater amount of dry gas produced in co-processing, the hydrogen yield was lower than that in pure VGO catalytic cracking. This suggests that H<sub>2</sub> is readily consumed in synergetic reactions that take place when both bio-oil and VGO components are present in the feed. As a result, more aromatics and coke are expected in the product pool of co-processing, which indeed has been observed in multiple studies.<sup>58,67</sup>

There are some discrepancies in the literature with respect to the yield of gasoline during co-processing. Fogassy et al.<sup>22</sup> indicated that HDO oil/VGO mixtures are expected to produce similar amounts of gasoline and LCO. Samolada et al.,<sup>58</sup> on the other hand, reported that more gasoline than LCO by up to 5 wt % was produced using the ReUSY catalyst during co-processing of hydrotreated bio-oil/LCO blends. This difference in observation can be largely attributed to the petroleum component of the blends used in each study, because LCO is known to yield less gasoline than VGO.<sup>58</sup> With regard to liquefied petroleum gas (LPG) (C<sub>3</sub>–C<sub>4</sub> compounds), less of it was produced during co-processing. This fraction was reported by Fogassy et al.<sup>22</sup> to be rich in propylene (~40%).



As previously mentioned, higher aromatic yields are expected during co-processing. This is mainly the case for the lighter monoaromatics, whereas the yields of di-, tri-, and tetra-aromatics obtained during co-processing were similar to those obtained during processing of pure VGO.<sup>22</sup> With the synergetic reactions taking place during co-processing that lead to enhanced formation of aromatics via hydrogen transfer, less olefins and more saturated compounds should be formed, as confirmed by Lappas et al.<sup>67</sup> Saturated compounds include normal- and isoparaffins and saturated naphthenes. It was observed that the latter two types of hydrocarbons increased during co-processing, whereas normal-paraffins actually decreased.<sup>58,67</sup>

**4.2.4. Coke.** The catalyst deactivation observed during the co-processing of HDO oil with petroleum-based fractions is not as severe or rapid as that witnessed during FCC of pure bio-oil feedstocks but is still quite substantial, even with bio-oils that have undergone hydrotreatment prior to the FCC step. This deactivation can be attributed to the decrease in coke precursor content as the bio-oil is diluted by petroleum-derived feeds.<sup>64</sup> Using this explanation, one would expect a higher coke yield during the co-cracking of HDO oil/VGO mixtures than with conventional FCC feeds. Indeed, Fogassy et al.<sup>22</sup> reported that more coke was formed during co-processing than during processing of pure VGO using an industrial FCC catalyst containing 15 wt % Y zeolites. Samolada et al.<sup>58</sup> reported that the addition of 15 wt % hydrodeoxygenated biomass flash pyrolysis liquid to LCO contributed to an increase in coke formation by over 50%. Similar trends were observed with the catalytic co-cracking of nonconventional hydrocarbon feeds with conventional feedstocks by Ng and Rahimi.<sup>68</sup> The challenge with excessive coke is that it can block the catalyst acid sites or lead to the blockage of the zeolite pores, which, in turn, leads to a decrease in the number of acid sites and causes significant diffusional restrictions inside the catalyst pores.<sup>34,69,70</sup> Such effects would exacerbate the mass-transport limitations, which are currently experienced with the catalytic cracking of heavier petroleum-derived feedstocks that contain larger molecules.<sup>31,71</sup>

It was also found that coke formation is not linearly related to the bio-oil content in the feed mixture, indicating that there is a certain level of interaction between bio-oil and its products on one hand and petroleum feeds and their products on the other.<sup>64</sup>

**4.2.5. Oxygenated Compounds.** To convert biomass-derived molecules into liquid fuels, oxygen must be removed as CO, CO<sub>2</sub>, or water, with the latter requiring hydrogen. Because no external hydrogen is provided during catalytic cracking, hydrogen is made available through reactions, including steam reforming, water–gas shift, and direct dehydrogenation of carbohydrates and hydrocarbons, as shown in Figure 3. These reactions lead to the formation of carbon oxides and coke.<sup>40</sup> The decomposition of oxygenated hydrocarbons occurs when either carbon–carbon bonds (decarboxylation) or carbon–oxygen bonds (decarbonylation) are broken or during water formation and hydrogenation reactions. It has been reported that decarbonylation is favored over decarboxylation for saturated hydrocarbons, whereas the latter is favored over the former for unsaturated hydrocarbons, such as those present in HDO oil. Therefore, when co-processing petroleum feedstocks with HDO oil, the formation of smaller oxygenated compounds, such as CO<sub>2</sub> and CO, is expected.<sup>72</sup> As in the case of pure pyrolysis bio-oils, the

products obtained from catalytic cracking of HDO oil/petroleum feedstock blends contain oxygenated compounds. As expected with oxygenated feeds like HDO oil, the yields of CO<sub>2</sub> and H<sub>2</sub>O increase rapidly with conversion of the feed blends. Not only does operating at higher temperatures result in a liquid oil product with a low oxygen content, but also the transfer of organic components from the aqueous phase to the oil phase is promoted, as suggested by de Miguel Mercader et al.<sup>64</sup> The formation of phenol and alkylphenol also increases at low conversions but starts to decrease at higher conversions, as reported by Fogassy et al.<sup>22</sup> This is because, at high temperatures (>500 °C), dealkylation and dehydroxylation, which lead to the formation of benzene and alkylbenzenes, are enhanced.

Carbon oxides in the gas product pool have been found to be in minimal concentrations compared to water. This indicates that most oxygen is converted into water rather than carbon oxides, as confirmed by several studies.<sup>21,50,51,64</sup>

Although the co-processing of upgraded pyrolysis oils in refineries constitutes a promising route toward the production of greener transportation fuels, several challenges have to be addressed before bio-oils can be co-processed in commercial FCC units. This remains as an important subject requiring further investigation.<sup>73</sup>

**4.2.6. Effect on Process.** Unlike processing pure bio-oil, no significantly negative effects on process operation have been observed during co-processing HDO oils with VGO. For example, while plugging was apparent during catalytic cracking of pure bio-oils, no plugging issues were encountered in co-processing experiments by de Miguel Mercader in a MAT unit using a FCC equilibrium catalyst at 520 °C and catalyst/oil ratios between 3 and 8.<sup>64</sup> This may be due to the fact that the bio-oils were upgraded prior to being co-fed with VGO. Blending of the two feeds, however, raises potential concerns. Although there are no accounts in the literature indicating compatibility issues with bio-oil/VGO blending, it has been reported that bio-oils from fast pyrolysis are insoluble in petroleum-derived fuels due to the high water content in the former. Thus, blending petroleum feedstocks with bio-oils requires the use of surfactants.<sup>65,74</sup> This may not be a significant issue because diesel and middle-distillate fractions are products of FCC and are not usually used as feedstocks.

**4.2.7. Summary.** (1) Lower catalytic cracking conversion is obtained with bio-oil/petroleum blends than with conventional FCC feedstocks. (2) Co-processing bio-oil with petroleum feedstocks yields more low-value dry gas than processing conventional FCC feedstocks. (3) Synergetic reactions take place during co-processing, leading to decreased formation of olefins but increased formation of aromatics and saturated compounds via hydrogen transfer. (4) Catalyst deactivation during co-processing of HDO oil with petroleum fractions is not as severe as that during cracking pure bio-oil feedstocks but is still quite substantial even when bio-oils are pre-hydrotreated. (5) Coke formation is not linearly related to the bio-oil content in the co-processed feed blend, indicating that there is interaction between bio-oil and petroleum components/their products. (6) The product from co-processing HDO oil and petroleum feedstock blends contains oxygenated compounds, such as phenols and alkylphenols. (7) Oxygen in the feed blend is mainly converted to water.

**4.3. Pure Vegetable Oils.** In the study of the catalytic cracking of pure vegetable oils and the co-cracking of petroleum feedstocks with these oils, whether edible or inedible, it is

important to understand the properties of the product streams generated and the effect of processing on standard refinery equipment, such as FCC units.

**4.3.1. Conversion.** Watkins et al.<sup>75</sup> performed catalytic cracking pilot plant runs using pure RSO and FCC equilibrium catalysts. They found that higher conversions of RSO were obtained compared to those attained using conventional FCC gas oil feedstocks. Similar results were achieved with pure palm oil and SBO. In fact, Dupain et al.<sup>34</sup> reported almost complete conversion of the triglycerides after only 1 s of reaction time and about 90% conversion of fatty acids after 5 s of reaction time during catalytic cracking of pure RSO. These higher conversions may be attributed to the fact that free fatty acid compounds are not diffusionally restricted in the catalyst pore network. Such compounds, which include C<sub>16</sub>- and C<sub>18</sub>-saturated straight-chain molecules, will therefore have relatively high diffusivities compared to the large-diameter aromatics and naphthenes that are present in conventional gas oil feeds.<sup>76</sup> Hence, fatty acid compounds can access the acidic active sites more frequently.

The high crackability of vegetable oils can also be attributed to their low thermal stability. It has been shown that pure crude palm oil undergoes thermal cracking by means of free radicals in the preheating zone of the FCC reactor.<sup>77</sup>

**4.3.2. Product Distribution.** While higher conversions were obtained in the catalytic cracking of pure vegetable oils compared to petroleum feedstocks, similar conclusions cannot be drawn with respect to gasoline yield, the primary product of FCC. It has been reported that less gasoline is produced with RSO, SBO, and palm oil than with conventional feeds. For instance, the gasoline yield could only reach up to 40–50 wt % during catalytic cracking of palm oil using either composite micro-/mesoporous zeolite catalysts or a commercial equilibrium catalyst, as reported by Sang et al.<sup>78</sup> and Melero et al.,<sup>61</sup> respectively. Taufiqurrahmi et al.<sup>79</sup> also reported the gasoline yield of 40 wt % using nanocrystalline zeolite beta catalysts. The gasoline yield from the catalytic cracking of conventional FCC feedstock is nearly 60 wt % in commercial FCC riser units.<sup>80</sup> In fact, Watkins et al.<sup>75</sup> indicate that the gasoline yield tended to be higher than the LCO yield when catalytically cracking vegetable oils, as shown in Table 8.

Despite the lower amount of gasoline produced, it has been reported that vegetable-oil-derived gasoline has higher research and motor octane numbers (RON and MON, respectively) than conventional gasoline, because of the presence of more

aromatics in the product pool.<sup>81</sup> In fact, Adjaye et al.<sup>82</sup> obtained a liquid product containing more than 95% aromatics in the cracking of canola oil with ZSM-5. Watkins et al.,<sup>75</sup> on the other hand, reported lower octane numbers for biogasoline produced from RSO, SBO, and palm oil cracking.

One particular advantage that vegetable-oil-derived gasoline has over conventional gasoline is its negligible contents of sulfur and nitrogen, as reported by Pinho et al.<sup>81</sup> This is expected because vegetable oils are not a significant source of either of these impurities.

The catalytic cracking of pure palm oil gives a total liquid product (TLP) yield of almost 80 wt % in some cases, with a significant portion of it (about 45–55 wt %) being LPG. This was achieved by Tani et al.<sup>44</sup> with an agitated flow reaction system and Katikaneni et al.<sup>83</sup> with a fixed-bed microreactor under atmospheric pressure and 400–500 °C. It is important to note that the experiments in these studies were conducted over excessive contact times, which may explain the higher yields of the lighter LPG fraction. Dupain et al.,<sup>34</sup> on the other hand, who used short contact times in a microriser reactor, achieved over 70 wt % TLP with only 3 wt % LPG. Buzetzki et al.<sup>84</sup> reported 85–90 wt % liquid product using a batch reactor, but the reaction times again were extensively long, ranging from 20 to 30 min. With respect to heavier products, Melero et al.<sup>38</sup> reported fairly low LCO and decant oil yields with a MAT unit, 10 and 2–3% of TLP, respectively.

Hydrocarbon distribution analysis by Tani et al.<sup>44</sup> with catalytically cracked palm oil at 430 °C showed that C<sub>15</sub> hydrocarbons were the predominant species in the liquid product, which came from the acid group of the triglyceride molecule. These results were obtained using both carbon and MgO-on-carbon catalysts. Other hydrocarbons, ranging from C<sub>7</sub> to C<sub>20</sub>, were observed in smaller quantities.

With regard to gas yields, catalytic cracking of pure vegetable oils produces a significant amount of gases. He et al.<sup>85</sup> reported 28–35 wt % vapor product during the cracking of ginger oil using MFI, BEA, and FAU zeolites in a fixed-bed reactor at temperatures between 350 and 400 °C. Similar results were achieved by Watkins et al.,<sup>75</sup> as shown in Table 8. While increasing the reaction temperature (500 °C) led to an increase in vegetable oil conversion,<sup>86,87</sup> the amount of gaseous products also increased significantly. In fact, the difference in gas yield between vegetable oil and petroleum cracking becomes even larger at such temperatures. This increase in gas production comes at the expense of the TLP yield, indicating that the liquid product is prone to overcracking at high temperatures.<sup>79</sup> Li et al.<sup>60</sup> performed catalytic cracking of pure CSO and observed that increasing the process severity, whether by increasing the reaction temperature, reaction time, or catalyst/oil ratio, increased the gas yield but decreased the yield of light fuel oil (<360 °C). This indicates that this product fraction is prone to overcracking into gases. As much as 30 wt % of dry gas was formed at a temperature of 500 °C, residence time of 90 s, and catalyst/oil ratio of 10.<sup>60</sup> He et al.<sup>85</sup> reported an increase in the vapor product yield, from 35 to 40 wt %, when the cracking temperature was increased from 400 to 450 °C.

With regard to the vapor product, it was reported that vegetable oil cracking gave higher C<sub>1</sub>–C<sub>2</sub> and propylene yields than conventional petroleum feedstocks under similar conditions, as reported by Watkins et al.<sup>75</sup> Bielansky et al.<sup>88</sup> reported that more hydrocarbon gases were produced with vegetable oils, such as RSO, SBO and palm oil, than with VGO.

**Table 8. Product Distribution Obtained from Catalytic Cracking of Various Vegetable Oils and VGO at 538 °C and Catalyst/Oil Ratio of 2<sup>75</sup>**

	rapeseed oil	soybean oil	palm oil	VGO
conversion (wt %)	81	79	80	66
hydrogen (wt %)	0.07	0.08	0.06	0.23
C <sub>1</sub> –C <sub>2</sub> (wt %)	2.3	2.6	2.4	1.3
C <sub>3</sub> –C <sub>4</sub> (LPG)	14.5	13.1	15.2	13.5
gasoline	47.3	44.8	44.3	49.5
light cycle oil	16.1	17.9	16.7	15.5
heavy cycle oil	1.9	2.0	2.1	14.4
bottoms	3.2	3.0	3.4	18.4
coke	2.6	2.9	2.6	1.1
MON	81.2	81.3	79.5	80.4
RON	93.0	93.4	91.7	92.8

The main components of the gaseous product were ethene and propene.

Results from FCC pilot riser runs with pure SBO and equilibrium FCC catalyst by Pinho et al.<sup>89</sup> showed that cracking at extremely high temperatures of 620 °C favored the formation of ethylene, whereas cracking at conventional FCC temperatures (580 °C) led to increased propylene production. Watkins et al.<sup>75</sup> also observed enhanced yields of lighter hydrocarbons ( $C_1$ – $C_3$ ).

A comparison between various vegetable oils shows that palm oil cracking produces more LPG (most of which is propylene) and light  $C_2$ – $C_4$  olefins than canola oil, SBO, and chicken fat. This is attributed to the higher concentrations of palmitic and stearic acids in palm oil.<sup>37</sup> Dry gas yields are also high, with ethylene being the predominant component (~90% of dry gases formed).<sup>44,83</sup> However, palm oil gives lower hydrogen yields than other vegetable oils, as presented in Table 8.<sup>75</sup>

**4.3.3. Oxygenated Compounds.** Water is the main oxygenated compound produced during the catalytic cracking of vegetable oils. It was reported that the amount of water formed during palm oil cracking using an equilibrium catalyst was about 10 wt %, almost twice that of CO and CO<sub>2</sub> combined (5 wt %).<sup>38</sup> Similar results were obtained by Marker<sup>90</sup> and Dupain et al.<sup>34</sup> Tani et al.,<sup>44</sup> on the other hand, observed that the amount of CO<sub>2</sub> generated was greater than that of water during palm oil cracking experiments, which could be attributed to the reaction system and the MgO-supported catalysts that promote decarboxylation of fatty acids. Water is formed via decarboxylation reactions, in which esters and fatty acids produce CO<sub>2</sub> as the byproduct.<sup>91</sup> Water can also be formed during catalytic dehydration reactions of fatty acids and esters.<sup>92</sup> Carboxylic gases, usually in the ratio of 60:40 for CO/CO<sub>2</sub>, can be produced via decarbonylation reactions from various oxygenated compounds, including ketones, aldehydes, fatty acids, and esters.<sup>91</sup>

**4.3.4. Catalysts.** The type of catalyst used in catalytic cracking of vegetable oil plays an important role with respect to conversion and overall product distribution. It has been reported that HZSM-5 catalysts gave a very high biogasoline yield during palm oil cracking,<sup>93</sup> because the high acidity of this material greatly enhanced cracking reactions over other reactions, such as hydrogen transfer. These acidic zeolites also promoted the cracking of palm oil to light olefins.<sup>94–96</sup> The superiority of HZSM-5 over other catalysts in the production of biofuels was confirmed by several comparative studies. Tamunaidu<sup>97</sup> reported that HZSM-5 was more active than microporous zeolite beta and produced more gasoline during cracking of crude palm oil. It has been observed that MCM-41 mesoporous materials provided favorable selectivities toward particular liquid hydrocarbons, such as gasoline, kerosene, or diesel. However, these catalysts gave lower conversion than HZSM-5.<sup>98</sup> The use of rare earth Y catalysts also promoted the formation of the organic liquid product, a significant portion of which was gasoline.<sup>86</sup> However, the conversion was also lower than that obtained using HZSM-5.

Silica–alumina catalysts have been shown to provide high conversions of vegetable oils, such as palm oil stearin and copra oil, and promote the formation of aromatics (~60 wt %) and aliphatic hydrocarbons in the kerosene boiling range (~30 wt %).<sup>99,100</sup> Zinc chloride catalysts have been reported to contribute to hydrogen-transfer reactions and the formation of hydrocarbons in the liquid phase. The addition of aluminum

to the catalyst also resulted in increased selectivity for biofuels.<sup>6,101</sup>

He et al.<sup>85</sup> compared the performance of different zeolites for cracking ginger oil at 400 °C. They reported that H-MFI zeolites provided a higher liquid product yield, including gasoline range hydrocarbons, compared to H-FAU and H-BEA zeolites, while H-FAU produced the highest amount of gaseous product and coke.

Spent catalysts have also been investigated during palm oil cracking. While the main gaseous hydrocarbon products of palm oil cracking are  $C_1$ – $C_3$  species, spent catalysts generate less of these compounds. Instead, they tend to result in a fairly large amount of isobutene, suggesting that reactions on spent FCC catalysts (solid acid) are of the ionic type, while those on fresh/equilibrium catalysts are of the radical type.<sup>44</sup>

**4.3.5. Effect on Process.** Issues with processing vegetable oil in FCC units are not as evident as in conversion processes that use fixed-bed reactors. The good feed–catalyst contact established in FCC riser units prevents problems associated with the formation of large amounts of residue that are likely to occur in fixed-bed reactors and cause plugging.<sup>77</sup>

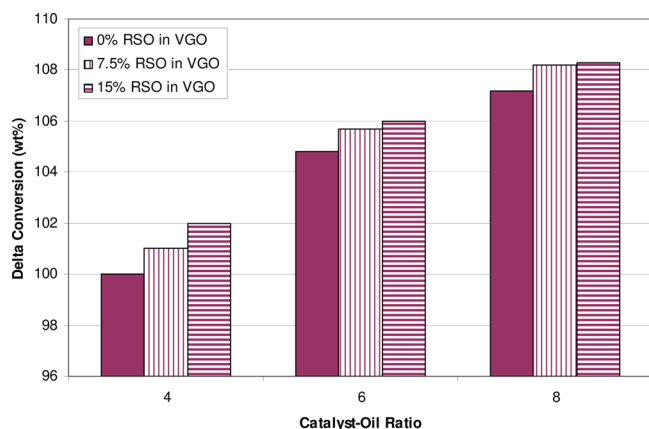
**4.3.6. Summary.** (1) Higher catalytic cracking conversion can be obtained with vegetable oils than with conventional FCC gas oil feedstocks at the same conditions, which is attributable to the low thermal stability and high diffusion rate in catalyst pores of the fatty acids in vegetable oils. (2) Catalytic cracking of vegetable oils generates less gasoline and more gas than conventional FCC feeds. However, vegetable-oil-derived gasoline has higher RON/MON and lower sulfur/nitrogen than petroleum gasoline. (3) Catalytic cracking of palm oil produces less gasoline and hydrogen but more LPG than canola oil, soybean oil, and chicken fat, because of the higher palmitic and stearic acid content in palm oil. (4) Water is the main oxygenated compound produced during catalytic cracking of vegetable oils. (5) Using HZSM-5 catalysts results in a higher biogasoline yield than other zeolite catalysts.

#### 4.4. Co-processing Vegetable Oils with Petroleum Feedstocks.

**4.4.1. Conversion.** Enhanced conversion was observed during catalytic cracking of blends of vegetable oil and conventional FCC feed compared to conventional feedstocks alone. This was confirmed by Watkins et al.<sup>75</sup> during FCC pilot plant studies in which 7.5 and 15% of various vegetable oils (RSO, SBO, or palm oil) in VGO–residue were catalytically cracked to achieve conversions 1–1.5 wt % higher than those obtained with the base VGO–residue feed. This increase in conversion may be attributed to the presence of triglyceride molecules in the palm oil, which reduce the concentration of difficult-to-convert aromatic species.<sup>38</sup>

Watkins et al.<sup>75</sup> also examined the effect of the catalyst/oil ratio on conversion. They obtained 1–2 wt % higher conversion with 7.5 and 15% mixtures of SBO in VGO–residue than with VGO–residue alone at a catalyst/oil ratio of 4. When the catalyst/oil ratio was increased to 8, the difference in conversion was decreased, while there was practically no difference in conversion between the 7.5 and 15% SBO feed blends.<sup>75</sup> Therefore, the effect of adding vegetable oils to the feed diminishes as the catalyst/oil ratio increases. These results are illustrated in Figure 10.

**4.4.2. Product Distribution.** The addition of vegetable oil to petroleum feedstocks has an apparent effect on the overall product distribution. Bielansky et al.,<sup>102</sup> using a ReUSY/ZXM-5 catalyst at 500–600 °C, reported that, as the concentration of RSO in the feed increased, the amount of dry gas produced



**Figure 10.** Effect of the catalyst/oil ratio on conversion of RSO/VGO blends during catalytic cracking.<sup>75</sup>

decreased, while gasoline yield remained fairly constant. However, the total fuel yield was lower by about 15 wt % compared to the yield obtained with pure VGO as a cracking feed. Increasing the concentration of RSO in the feed blend also increased the amount of LCO and residue produced.<sup>34,102</sup> Similar results were achieved by Watkins et al.<sup>75</sup> and Melero et al.,<sup>38</sup> who observed that the product distribution was affected considerably by the amount of vegetable oils in the feed. As the content of SBO in the feed is increased, the yields of gasoline, LCO, and decant oil tend to proportionally decrease, while the yields of dry gas, LPG, and water tend to proportionally increase. Melero et al.<sup>38</sup> also reported similar trends in co-processing palm oil with VGO, especially at higher cracking temperatures (565 °C). The triglyceride-based components of the feed mixture led to a reduced liquid product yield, especially for the LCO and decant oil fractions.<sup>38</sup> Watkins et al.,<sup>75</sup> on the other hand, observed increases in propylene, gasoline, and LCO yields and a reduction in dry gas and hydrogen yields when more SBO, RSO, or palm oil was blended into conventional petroleum feedstocks.

The yield response to the addition of vegetable oil into FCC feedstocks also depends upon the properties of the base FCC feed. It was observed that the addition of RSO into a hydrotreated VGO feed resulted in more gas and coke at similar conversions than when blending RSO into a non-hydrotreated feed, whereas the addition of RSO to a composite feed produced less gas and coke at similar conversions.<sup>75</sup> Graça et al.<sup>103</sup> confirmed in a model compound study that the interaction of oxygenated compounds with hydrocarbon compounds depended upon the types of these hydrocarbons. They showed that, when catalytically cracked, phenol in *n*-heptane produces more coke than phenol in methycyclohexane. This conclusion may be extended to the cracking of vegetable oils with two types of petroleum feedstocks, one that is highly naphthenic and the other that is highly paraffinic.

The effect of different types of vegetable oil blends with petroleum feedstocks on cracking product distribution was studied by Bielansky et al.<sup>88</sup> using a commercial E-CAT in a continuous FCC pilot plant. Blends of VGO with RSO, SBO, and palm oil were investigated, with these blends containing 20–100% vegetable oils. It was observed that the gasoline yield remained constant for the different feeds, ranging between 40 and 43 wt %. The yield of vapor product, however, was the highest with the palm oil/VGO blend and the lowest with the RSO/VGO blend. As for LCO and residue products, the

highest amount was produced with the SBO/VGO blend and the lowest amount was produced with the palm oil/VGO blend. These differences in the product yields were more pronounced as the concentration of vegetable oil in the blends was increased. Buzetzki et al.,<sup>104</sup> on the other hand, did not observe differences in product yields and properties when cracking RSO, SBO, sunflower oil, and jatropha oil feeds with various catalysts (NaY, clinoptilolite, and HZSM-5). This might be attributed to the fact that the cracking was performed under very mild temperatures in a batch reactor.

Process conditions also significantly affect the product distribution obtained from the catalytic cracking of mixtures of vegetable oils and petroleum feedstocks. As the process severity is increased, by increasing the catalyst/oil ratio for instance, higher gas and coke yields are obtained while lower amounts of LCO and decant oil are produced.<sup>38</sup> The maximum gasoline yield is also highly dependent upon the catalyst/oil ratio. Melero et al.<sup>38</sup> reported that processing pure palm oil provided a maximum gasoline yield with a catalyst/oil ratio of 2, whereas co-processing 30% palm oil in VGO provided a maximum gasoline yield with a catalyst/oil ratio of 3. These results are different from those obtained when pure VGO is cracked, during which no maximum is observed.

As in the case of catalytic cracking of conventional FCC feeds,<sup>105</sup> increasing the reaction time and temperature during co-processing increases the amount of light fractions and decreases the amount of heavy fractions produced. Dupain et al.<sup>34</sup> reported higher dry gas and gasoline yields and lower heavy cycle oil (HCO) and LCO yields when the cracking temperature was increased from 465 to 525 °C using a commercial E-CAT. Furthermore, it was observed that, while dry gases and gasoline were formed almost immediately at the onset of cracking experiments, the dry gas yield remained constant as the reaction time was increased. At the same time, the gasoline yield continued to increase with very limited overcracking. The LCO yield, on the other hand, hardly changed when the residence time was longer than 3 s.<sup>34</sup>

With regard to gasoline quality, it has been reported that gasoline obtained from co-processing of RSO with petroleum feedstocks was essentially oxygen-free with significantly increased RON and slightly increased MON as the RSO concentration in the feed blend was increased.<sup>102</sup> This was also the case when SBO was used in the blend.<sup>38</sup> However, other studies suggested that the octane number of gasoline, especially MON, obtained from biofeed mixtures was consistently lower than that obtained from petroleum feeds because of the lower aromatics content in the former.<sup>75</sup> Analysis of the paraffins, isoparaffins, olefins, naphthenes, and aromatics (PIONA) composition of gasoline produced from co-processing showed that the contents of aromatics and unsaturated naphthenes increased when more RSO was blended into the feed, while the contents of saturated naphthenes, *n*-olefins, and isoparaffins tended to decline.<sup>102</sup> The higher aromatics content in gasoline obtained by co-processing is due to the higher aromatization rate of the unsaturated fatty acids because of the presence of double bonds in the molecular structure. Hence, vegetable oils that have a significantly higher content of unsaturated fatty acids, such as RSO, produce more aromatic gasoline. In fact, as much as 40 wt % aromatics was obtained in gasoline and in the TLP.<sup>34</sup> This increase in aromatics content supports the observations made by Bielansky et al.<sup>102</sup> with respect to the higher octane numbers in the gasoline obtained by co-processing. Melero et al.<sup>38</sup> also suggested that, under severe

experimental conditions (565 °C and 12 s reaction time), olefins had a tendency to undergo frequent cyclation, aromatization, and condensation reactions, which led to their conversion into aromatics and coke. This observation is supported by the higher aromatic yield obtained during co-processing of palm-oil-based biofeeds. The increase in aromatics observed by Melero et al.<sup>38</sup> mostly involved mono- and diaromatics, which ended up in the gasoline fraction and further enhanced the octane number. Melero et al.<sup>38</sup> did, however, report a decrease in polyaromatics formation, which is due to the lack of presence of these compounds in palm oil and all other vegetable oils. Hence, polymerization reactions are limited. These observations were confirmed by catalytic cracking experiments conducted by Dupain et al.<sup>34</sup> using pure oleic acid and saturated stearic acid. Their results suggested that saturated stearic acid was the main contributor to enhanced gasoline and gas yields during co-processing. Moreover, much less aromatics and much more isoparaffins and iso-olefins were obtained with stearic acid than with oleic acid, indicating that oleic acid, as well as other unsaturated fatty acids, such as linoleic and linolenic acids, are responsible for aromatics formation.

The lighter components in the gasoline fraction ( $C_5$ –90 °C) tend to increase with higher concentrations of palm oil in the feed, whereas the heavier components (90–221 °C) tend to decrease. This is because most fatty acid molecules in palm oil are similar in length to molecules in LCO and are easily cracked. Moreover, because decant oil ( $C_{18}$ – $C_{30}$ ) is heavier than LCO, its formation is mainly via polymerization reactions, which are quite rare in the case of fatty acids.<sup>38</sup>

The composition of dry gas is also affected by the presence of biofeed. Saturated  $C_3$ – $C_4$  hydrocarbon compounds have been reported to decrease when the RSO concentration in the feed is increased. All other gases, such as methane, ethane, ethylene, propylene, and butenes, tend to increase when more RSO is present in the feed.<sup>34,102</sup> Moreover, it has been suggested that the presence of vegetable oils in the feed enhances olefin production compared to petroleum-derived feedstocks. This is due to hydrogen transfer from hydrocarbon molecules to the available oxygen to form water.<sup>106</sup>

**4.4.3. Coke.** There are some discrepancies in the literature as to whether the addition of RSO into conventional feedstocks increases or decreases the amount of coke formed. Watkins et al.<sup>75</sup> reported that significantly less coke per unit conversion was formed with a 7.5% RSO in VGO–residue feed than that with a pure VGO–residue. They also indicated that other types of vegetable oils (such as palm and soybean) at the same concentrations also resulted in lower coke yields than the pure VGO–residue feed but not lower than that achieved by co-processing with RSO. Using 7.5% palm oil in the VGO–residue mixture, for instance, produced almost 1 wt % less coke than using conventional VGO–residues at the same conversion. Moreover, it was reported that increasing the content of vegetable oil in VGO–residue mixture to 15% further reduced the amount of coke formed for a given conversion.<sup>75</sup> Work by other researchers, however, showed that coke formation increased by as much as 6 wt % as the RSO content in the mixture increased.<sup>34,102</sup> These opposite trends in coke yield might be attributed to the differences in the petroleum feedstocks used by each research group, since product yields in co-processing depend upon the properties of FCC feed, as previously discussed. The higher coke yields obtained by Watkins et al.<sup>75</sup> are most likely due to the heavy residue in the

feed, which typically contains large aromatic molecules that behave as coke precursors. Adding vegetable oil to this heavy feedstock dilutes the aromatic molecules and reduces the probability of coking by polymerization and condensation. However, this might not be the case with the other two studies in which only VGO was used as the petroleum component. Moreover, most of the coke is formed in the initial stage of residue cracking because some of the large free radicals formed by thermal cracking are not able to penetrate catalyst pores and, hence, are deposited on the catalyst external surface.<sup>107</sup>

**4.4.4. Catalysts.** The choice of catalyst is also a major factor influencing the product distribution. Dupain et al.<sup>34</sup> investigated the effect of ZSM-5 as an additive to an E-CAT. It was found that using E-CAT with ZSM-5 resulted in higher gas yield but lower LCO and gasoline yields compared to using E-CAT alone. The addition of ZSM-5 proved to enhance the catalytic cracking of biomass-derived feedstocks, as previously discussed.

It was also reported that HZSM-5 gave the highest amounts of organic liquid products compared to other catalysts, such as H–mordenite, H–Y, silicalite, aluminum-pillared clay, and silica–alumina catalysts, in the catalytic conversion of canola oil to biofuels.<sup>99</sup> However, aluminum-pillared clay gave the highest amount of olefins in the gaseous product.<sup>99</sup>

**4.4.5. Oxygenated Compounds.** It has been widely reported that water is the primary deoxygenated product when co-processing petroleum-based feedstocks with vegetable oils, especially when rapeseed or canola oil are used.<sup>94</sup> Bielansky et al.<sup>102</sup> observed the yield of water to be 13 times that of  $CO_2$ , with such a difference increasing when larger concentrations of RSO were used in the feed. In a separate study, Bielansky et al.<sup>88</sup> reported that almost 20 times more water than carbon dioxide was formed when mixtures of RSO, SBO, and palm oil with VGO were cracked in a FCC pilot plant. While oxygenates in the feed may evolve as gaseous products (i.e., carbon oxides), they may also be transformed into liquid products, such as ketones, aldehydes, carboxylic acids, and furans, at low levels.<sup>34,38,108</sup> Watkins et al.,<sup>75</sup> however, did not observe any oxygenated compounds in their liquid product.

The effect of the vegetable oil concentration in co-processed feedstocks on the amount of oxygenated compounds generated is no different from that of any other biomass-derived feedstocks. Melero et al.<sup>38</sup> observed that increasing the palm oil concentration in VGO increased the formation of oxygenated compounds, as expected.

**4.4.6. Summary.** (1) Higher catalytic cracking conversion can be obtained with vegetable oil and petroleum feedstock blends than with conventional FCC feeds. (2) Product distribution is affected considerably by the relative amount of vegetable oil added to co-processed blends. As the content of vegetable oil in the feed increases, the yields of gasoline, LCO, and decant oil proportionally decrease, while those of dry gas, LPG, and water proportionally increase. (3) The product yields from co-processing also depend upon the properties of the petroleum FCC feedstock. (4) Minor differences in product distribution and composition are observed among various vegetable oils blended with the same petroleum feedstock. These differences become more pronounced when the amount of vegetable oil component in the blend increases and/or when higher reaction temperatures are used. (5) Gasoline from catalytic cracking vegetable oils with a higher content of unsaturated fatty acids, such as RSO, has a higher content of aromatics and, consequently, a higher RON/MON than other

vegetable-oil-derived gasolines. (6) The oxygen in feed blends is mainly converted to water. However, it may be transformed into carbon oxides or liquid compounds, such as ketones, aldehydes, carboxylic acids, and furans, at low levels.

**4.5. WCO.** Although the use of WCO has a number of advantages from an environmental perspective, the catalytic cracking of these oils has been explored minimally in published studies. Taufiqurrahmi et al.<sup>109</sup> conducted catalytic cracking tests using a waste cooking palm oil (WCPO) with various nanocrystalline zeolite (ZSM-5, Y, and beta) catalysts in a fixed-bed reactor at 400–500 °C. The conversion of WCPO ranged from 87 to 92 wt %, with the ZSM-5 zeolite catalyst providing the highest conversion and the beta zeolite catalyst providing the lowest conversion. Results showed that the optimal reaction temperature for the maximum yield of organic liquid product (OLP) was around 460 °C. At higher temperatures, the OLP yield was lower because of overcracking reactions, resulting in an increased yield of gaseous product. The yield of the gasoline fraction produced within the OLP was also the highest, ranging from 33 to 37 wt % at the same temperature.

Melero et al.<sup>38</sup> investigated co-processing of WCO with VGO using a MAT unit with an industrial FCC equilibrium catalyst. It was observed that gasoline, LCO, and decant oil yields dropped with an increasing WCO content in the feed. The gasoline yield was decreased from 47 to 40 wt %, whereas the LCO and decant oil yields were reduced from 20 to 12 wt % and from 9 to 3 wt %, respectively, as the WCO content was increased from 0 to 100% in the feed. However, there was a slight increase in LPG. As the amount of TLP was decreased when the amount of WCO in the feed was increased, the total aromatics content was increased, with most of the aromatics ending up in the gasoline fraction, resulting in a higher gasoline octane number.<sup>38</sup>

Water formation during catalytic cracking of WCO is significant. As indicated by Melero et al.,<sup>38</sup> almost 5 wt % water was formed in co-processing 30% WCO in VGO and 11 wt % water was formed in cracking pure WCO.

Nam et al.<sup>110</sup> compared the catalytic cracking of vegetable oil sludge to pyrolysis of the same material. This sludge, a byproduct of vegetable oil processing factories, consisted of 61% triglycerides, 37% free fatty acids, and 2% impurities. It was concluded that the catalytic cracking of the sludge in a MAT unit with a ZSM-5/MCM-41 catalyst was more “efficient” than the pyrolysis of the sludge because significantly higher conversion (82 versus 57 wt %) and selectivities for LPG (31 versus 17 wt %) and gasoline (42 versus 29 wt %) were attained from catalytic cracking. It also produced much less coke (3 versus 19 wt %) and dry gas (7 versus 9 wt %) than pyrolysis.<sup>110</sup>

**4.6. Animal Fats.** As mentioned earlier, only a few studies have examined the catalytic cracking of animal fats. Melero et al.<sup>38</sup> conducted catalytic cracking tests using pure animal fat as well as blends of it with VGO in a MAT unit with an equilibrium catalyst. Tian et al.<sup>37</sup> tested a blend of chicken fat and VGO as cracking feedstock for a two-stage riser FCC unit containing Y and ZSM-5 zeolite catalysts.

Conversion of animal fats tends to be exceptionally high, reaching almost 95 wt %, with the product consisting of dry gases, LPG, gasoline, diesel oil, heavy oil, and coke.<sup>37</sup> Therefore, the higher the concentration of fat in the feed, the higher the overall feed conversion that can be achieved.

It was found that the LPG yield was increased with increasing concentrations of animal fat in the VGO feed, while the

gasoline, LCO, and decant oil yields were decreased. Melero et al.<sup>38</sup> observed that changes in the yield of LPG (from 18 to 23 wt %), gasoline (from 47 to 39 wt %), LCO (from 20 to 10 wt %), and decant oil (from 9 to 2 wt %) took place as the animal fat concentration in the feed was increased from 30 to 100%. This trend is expected because triglyceride-based biomass feedstocks lack aromatics and refractory compounds. The limited amount of aromatics in the feed reduces the yield of liquid products, especially LCO and decant oil, and enhances the formation of gases. Such trends are even more pronounced in the case of animal fats, since they consist mainly of saturated fatty acids.<sup>38</sup>

Despite the limited amount of aromatics in animal fats, the gasoline produced from catalytic cracking of animal fat contained a significant amount of aromatics, as confirmed by Melero et al.,<sup>38</sup> who observed an increase in aromatics content in gasoline (60–70 wt %) with increasing animal fat concentrations in VGO. Consequently, a high octane number was achieved (RON was above 95). High concentrations of both C<sub>7</sub>–C<sub>9</sub> aromatics and C<sub>5</sub>–C<sub>6</sub> olefins in gasoline were detected, with the total reaching almost 85 wt %.<sup>37,111</sup> The high aromatics concentration in gasoline can be attributed to either the aryl groups in the feed, which remain unchanged after cracking, or the aromatics that are produced via hydrogen-transfer, cyclization, and aromatization reactions.<sup>37</sup> To further increase the aromatics content in the product pool, pyrolysis catalysts should be used proportionally to conventional FCC catalysts, since the former is known for promoting cyclization and aromatization reactions.<sup>112</sup>

The assessment of the properties of biogasoline produced from catalytic cracking of animal fat revealed that the levels of gum, sulfur, aromatics, and benzene were acceptable. However, copper strip corrosion values and the induction period because of the effect of residual oxygen in the gasoline were quite high. The produced biodiesel, on the other hand, had acceptable acidity, copper strip corrosion values, oxidation stability, color, solidifying point, kinematic viscosity, and distillation range.<sup>37</sup>

As expected, the amount of water formed during the catalytic cracking of animal fat is also influenced by the concentration of fat in the feed. Melero et al.<sup>38</sup> reported that the water yield increased from 3 to 12 wt % when the animal fat concentration in the feed went from 30 to 100%. The amounts of water and CO<sub>2</sub> formed during the catalytic cracking of animal fats are greater than those formed during the processing of vegetable oils, particularly palm oil and SBO.<sup>37</sup>

**4.7. Oxygenated Model Compounds.** Extensive work has been dedicated to the study of individual model compounds.<sup>40,57,103,113–116</sup> These studies, which involve the development of reaction mechanisms and kinetic models as well as parameter estimation, offer an important understanding of the fundamentals of processing actual complex biofeedstocks. However, they provide only partial information on the reaction pathways and ignore the interaction between various groups of compounds during processing.<sup>5</sup> Hence, the focus of the present review will be limited to research performed using mixtures of multiple model compounds to represent actual biomass-derived feedstocks, because such work represents a more realistic approach to understand the processing of these biofeedstocks.

A number of studies have investigated the formation of undesirable species during the catalytic cracking of mixtures of model compounds to identify these oxygenated compounds and eliminate them via pyrolysis before processing in FCC units. Gayubo et al.<sup>117</sup> performed catalytic cracking with two

mixtures of oxygenated compounds in a fixed-bed reactor using HZSM-5 zeolites. The mixtures, which contained one model compound as a representative for each major class of oxygenates, consisted of acetone, acetic acid, methanol, 2-butanol, phenol, and acetaldehyde (mixture 1) and acetone, acetic acid, 2-methoxyphenol, 2-propanol, and furfural (mixture 2). The authors discovered that catalyst deactivation was extremely rapid and, consequently, the amount of product decreased rather quickly. Furthermore, the reactor inlet ducts were blocked by carbonaceous deposits that were formed during the reaction by thermal degradation of either furfural or methoxyphenol or polymerization of the two compounds. This shows that one cannot draw correct conclusions using individual model compounds, because the presence of other compounds may affect the conversion of all species in the feed.

The presence of certain ketones, such as acetone, in model compound mixtures also results in severe and irreversible catalyst deactivation due to the formation of coke that selectively blocks the most acidic sites.<sup>40,73</sup> Carboxylic acids and alcohols, such as acetic acid and isopropyl alcohol, may also cause catalyst deactivation, although the deactivation might be partly reversible.<sup>40</sup> Moreover, glycerol solutions were also found to give a significantly increased amount of coke compared to VGO during catalytic cracking.<sup>40</sup> Because most oxygenated compounds might contribute to the formation of coke,<sup>73</sup> it would be desirable to pre-separate certain components, mainly oxyphenols, furfural, ketones, and their derivatives, before converting bio-oil into hydrocarbons on acidic catalysts.<sup>117</sup> Pre-FCC separation of ketones was also recommended by Guo et al.<sup>118</sup> after examining the role of ketone components in pyrolysis bio-oil during catalytic cracking with mixtures of ketone model compounds. It was found that ketones with smaller molecular weights were cracked easily, while those with larger molecular weights were more difficult to convert.

The interactions between various types of oxygenated model compounds were also investigated to determine which type of species has the greatest impact on conversion and product selectivity. Conversion and reactivity of phenols have been found to be quite low when they are mixed with other types of components and their converted products.<sup>5,57,119</sup> On the other hand, some compounds may promote the conversion of other species. For instance, Gayubo et al.<sup>113</sup> reported that the presence of acetone in the feed enhanced the conversion of acetic acid because of the autocatalytic effect of acetone.

Understanding the effects of oxygenated compounds on conventional gas oil feedstocks during co-processing is also important. Corma et al.<sup>40</sup> studied several mixtures of VGO with glycerol solution in a MAT unit at 500 °C using various catalysts, including E-CAT, Al<sub>2</sub>O<sub>3</sub>, USY zeolite, ZSM-5, and SiC. They found that increasing the concentration of glycerol in the feed reduced the conversion. Moreover, the addition of glycerol affected the gasoline yield negatively but increased the LCO yield slightly. The authors explained these results in terms of the dilution effect of glycerol when it was mixed with VGO. Graça et al.,<sup>119</sup> on the other hand, observed increases in overall conversion as well as fuel gas, LPG, and gasoline yields with mixtures of standard gas oil and different oxygenated compounds, including acetic acid, hydroxyacetone, and phenol, using the E-CAT/ZSM-5 catalyst. It was found that the conversion of gas oil itself (within the mixture) was not altered significantly by the presence of the oxygenated model compounds. The reason for the higher gasoline yield obtained

by Graça et al.<sup>119</sup> than that obtained by Corma et al.<sup>40</sup> might be due to the presence of phenols, since these compounds tend to undergo dehydration to form benzene, a component of gasoline. However, this increase in the gasoline yield was compromised by the reduced gasoline quality caused by benzene.<sup>119</sup>

As previously discussed regarding the co-processing of bio-oils and petroleum feedstocks, the hydrogen produced during cracking is also consumed in synergetic reactions. This was also observed during the catalytic cracking of glycerol–VGO mixtures, because less hydrogen was produced in comparison to the cracking of pure VGO or pure glycerol solution.<sup>40</sup> Moreover, Pinho et al.<sup>89</sup> performed experiments with 20% ethanol in gas oil and concluded that blending ethanol with gas oil favored ethane production, whereas pure ethanol processing favored ethylene production. This indicates that the intimate contact between ethanol and gas oil interfered with the dehydration reactions and promotes hydrogen transfer from gas oil to dehydrogenation products. Furthermore, the yields for both CO and CO<sub>2</sub> obtained during the conversion of glycerol–VGO mixtures were lower than expected, which supports the hypothesis of the existence of a synergetic effect during the co-processing of oxygenated compounds with petroleum gas oils.<sup>40</sup>

With regard to carbon oxides, it was shown by Graça et al.<sup>119</sup> that acetic acid and gas oil mixtures provided higher yields of CO<sub>2</sub> and CO than mixtures of gas oil with either hydroxyacetone or phenol. This suggests that carboxylic acids are the major contributors to the formation of these gases.

A strong interaction between oxygenated compounds and FCC zeolite catalysts, such as ZSM-5, was also observed during the catalytic cracking of model bio-oil compound mixtures with conventional feeds. Graça et al.<sup>119</sup> conducted catalytic cracking with mixtures of standard gas oil and various oxygenated compounds in a lab-scale unit under relevant FCC conditions using an equilibrium catalyst with and without a ZSM-5 additive. They observed that the gas oil feed was preferentially adsorbed on the catalyst over the oxygenated compounds prior to the addition of ZSM-5. After introducing ZSM-5, the trend was reversed, with the oxygenates being preferentially adsorbed on the catalyst. As a result, the role of ZSM-5 became less important in the presence of oxygenated compounds for the conversion of olefins in the gasoline fraction into lighter fractions.<sup>119</sup>

## 5. CONCLUSION

The decline in conventional crude oil, increasing global energy demand, and current legislature mandating the minimization of the carbon footprint associated with fuel production have propelled studies in evaluating the options of processing biomass materials to produce biofuels. In fact, studies on processing these materials using conventional technologies have been expanded quite rapidly over the past decade. The current review summarizes research work conducted in the area of fluid catalytic cracking of biomass-derived feedstocks to assess the viability of using existing refinery operations to generate biofuels.

Most of the literature has focused on the processing of pyrolysis bio-oils, while some of the literature has addressed the catalytic cracking of vegetable oils. A few studies have examined the cracking of waste oils and animal fats. The nature and properties of the biomass-derived oils play an important role in the FCC process, especially with respect to conversion, product distribution and yields, operations, and catalyst activity. Because

of their complexity and unstable nature, pyrolysis bio-oils tend to cause severe problems during FCC operation. Co-processing petroleum feedstocks with bio-oils leads to significant formation of undesirable products (coke, tar, char, etc.), irreversible catalyst deactivation, and reactor plugging. Hence, pyrolysis oils may require hydrotreatment prior to processing or co-processing in FCC units. Moreover, there are substantial differences in product distributions obtained from the catalytic cracking of bio-oil/petroleum mixtures versus pure petroleum feeds, because the former provides more low-value dry gases and less TLP than the latter. In addition, biogasoline generated from pyrolysis oils is highly aromatic.

The catalytic cracking of vegetable oils yields more total hydrocarbon liquid product, especially gasoline, than the cracking of pyrolysis bio-oils. Therefore, vegetable oils are advantageous over pyrolysis bio-oils from a catalytic cracking perspective.

With regard to co-processing, it has been shown that conversion, product distribution, and product quality are significantly affected by the presence of vegetable oils in conventional FCC feeds. Co-processing vegetable oils with petroleum feedstocks generally produces less liquid fuel products (gasoline and diesel) but improves product quality (high octane and cetane numbers). The use of the HZSM-5 catalyst as an additive/catalyst is effective to upgrade biomass-derived oils for enhanced production of organic distillates and fuels.

Although several studies have investigated the catalytic cracking of biomass-derived oils and their blends with conventional petroleum feedstocks, there are still important knowledge gaps to be filled in this research area to achieve commercial application. These gaps include but are not limited to compatibilities of different bio-oils with conventional petroleum feedstocks, the effects of bio-oil species on competing FCC reaction mechanisms, and the heterogeneous kinetic modeling of the catalytic cracking of bio-oil/petroleum feedstock mixtures. All of these are directly related to the design and operation of commercial FCC units.

Another equally important research subject is the hydro-processing of bio-oils and their blends with conventional petroleum feedstocks. A separate review has been conducted by the authors to summarize the related research progress and findings in the last 2 decades.

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### Notes

The authors declare no competing financial interest.

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## NOMENCLATURE

ACE = advanced cracking evaluation  
 BTY = billion tons per year  
 CSO = cottonseed oil

E-CAT = equilibrium catalyst  
 FCC = fluid catalytic cracking  
 GHG = greenhouse gas  
 H/C = hydrogen/carbon ratio  
 HCO = heavy cycle oil  
 HDO = hydrodeoxygenation  
 LCO = light cycle oil  
 LPG = liquefied petroleum gas  
 MAT = microactivity test  
 MCR = micro carbon residue  
 MON = motor octane number  
 OLP = oil liquid product  
 PERD = Program of Energy Research and Development  
 PIONA = paraffins, isoparaffins, olefins, naphthenes, and aromatics  
 RON = research octane number  
 RSO = rapeseed oil  
 SBO = soybean oil  
 TLP = total liquid product  
 VGO = vacuum gas oil  
 WCO = waste cooking oil  
 WCPO = waste cooking palm oil

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