

BIOFUEL PRODUCTION FROM THERMOCATALYTIC PROCESSING OF VEGETABLE OILS: A REVIEW

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ABSTRACT

With the worsening environmental problems caused by the greenhouse effect, the study of fuel alternatives generated by non-fossil sources has intensified. The incorporation of biodiesel (mono-ester of triglycerides) to petroleum diesel is an example of commercial application for reduction in the emission of fossil CO₂ and SO_x and NO_x as well. In this context, the generation of mixture of hydrocarbons for catalytic cracking of vegetable oils combines the advantages of the Transesterification process to generate compounds such as petroleum-derived fuels such as: gasoline, kerosene and diesel. This review presents current trends in scientific literature for biofuels from thermal (pyrolysis) and catalytic processing. For the pyrolysis it has been described the temperatures use to obtain the fuel in the diesel range. The catalytic processing involves the heterogeneous catalysts used in the processing crude oil and the conditions of temperature and pressure. In conclusion it is showed that the cracking catalytic process allows chose what fuel does one want simply changing the catalytic that is used.

Keywords: Biofuels, Pyrolysis, Hydroprocessing, Vegetable oils.

PRODUCCIÓN DE BIOCOMBUSTIBLES POR MEDIO DE LOS PROCESOS TERMOCATALÍTICOS DE ACEITES VEGETALES: UNA RESEÑA

RESUMEN

Con el empeoramiento de los problemas ambientales causados por el efecto invernadero, el estudio de combustibles alternativos generados por fuentes so fósiles ha sido intensificado. La incorporación de biodiesel (mono-éster de triglicéridos) a diesel de petróleo es un ejemplo de una aplicación comercial para la reducción en la emisión de CO₂ fósil, SO_x al igual que NO_x. En este contexto, la generación de mezclas de hidrocarburos para craqueo catalítico de aceites vegetales combina las ventajas de los procesos de Transesterificación para generar componentes como los combustibles derivados del petróleo, como: gasolina, kerosene y diesel. Esta reseña presenta las tendencias actuales en la literatura científica para procesos térmicos (pirolisis) y catalíticos en los biocombustibles. Para la pirolisis se han descrito las temperaturas usadas para obtener el combustible en los rangos de diesel. Los procesos catalíticos implican los catalizadores heterogéneos usados en el procesamiento del crudo y las condiciones de presión y temperatura. En conclusión se muestra que el proceso de craqueo catalítico permite elegir que combustible puede buscarse simplemente cambiando la catálisis que es usada.

Palabras clave: Biocombustibles, Pirolisis, Hidroprocesamiento, Aceites vegetales.

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INTRODUCTION

Among the primary energy consumed on the planet, it is estimated that 80% is obtained from fossil sources and non-renewable gases in the atmosphere and the need for sustainable development, in the long run, the use of renewable fuels has gained importance. One of the key market niches for these alternative forms of energy is the transportation sector, which accounts for more than half of the consumption of non-renewable energy sources (Salvi, Subramanian, & Panwar, 2013). In this way, one of the main topics of research in relation to renewable energies must be the development of fuels suitable for use in Otto and Diesel engines. The more similar are the alternative to fossil fuels, the easier it will be to replace.

The most of fossil energy is consumed in transportation. The direct use of vegetable oils in engines was an option during the historic oil crises. However, several downside are related to that application in an engine built to run on diesel, features like low cold flow, high viscosity which hinder the atomization, low energy density, corrosion of resources. As a result of emissions of greenhouse motors, carbon deposition in the cylinders, low life time, besides the easy oxidation (Casas, Ramos, & Pérez, 2011b). The direct employment in engines is possible, if the engine is adapted for the same, but it is impossible to change all the fleet of a country to operate only with vegetable oil (Casas, Ramos, & Pérez, 2013).

By the great difficult of using vegetable or animal fatty in conventional internal combustion engines, the search for the adaptation of the same combustion technology, led to several rendering techniques. The technique of biodiesel presented an alternative to the various difficulties of the direct combustion of vegetable oil, but failed to resolve all the problems. On the other hand, the thermal and catalytic processing of vegetable oils is a very attractive option for the market. Their products are identical to those obtained by petroleum cracking, which is doubly advantageous for the direct application in conventional internal combustion engines and for integration with the petrochemical industry, without requiring a dramatic adaptation of the process. To obtain petrochemical inputs can be made with vegetable oils, edible or not (Casas, Ramos, & Pérez, 2011a), In addition they can be applied in residual oils of plants and sewers (Kwon, Yi, & Jeon, 2014), as well as animal fatty.

1. HIGH TEMPERATURE PROCESSING

The thermal processing could be classified by the reaction desired. If reducing the carbonic chain is the main objective, the cracking should occur, however, if the remove of oxygen from the free fatty acids is the main objective, the deoxygenation process should occur. Because the high temperature processing of triglycerides, neither of this process occur separately. In the cracking, the fragmentation take place primarily over the deoxygenation, but the deoxygenation process also occurs. The inverse occurs on deoxygenation, where the cracking also occurs by several factors.

The main objective of this section is to evaluate the literature works that process vegetable oil and its components on high temperature, looking for oil raw material, catalysts, reactors and the conditions are available.

1.1 THERMAL PROCESSING (PYROLYSIS)

Pyrolysis is a process where organics compounds are exposed at high temperature and in consequence of that, they crack. To vegetable oil it begins at about 593 K (Biswas & Sharma, 2013). As the next step, the cracking of resulting molecules and deoxygenation occur simultaneously, by thermal effects. This process was widely studied and several reviews is available on literature (Fréty et al., 2011; K. D. D. Maher & Bressler, 2007; Shay, 1993).

Historically, the first works involving thermal cracking of renewable oil are from the beginning of the XX century, where the “Universal Oil Products Company, Chicago US” reported the pyrolysis of cottonseed oil (Egloff & Morrell, 1932) and also of seal oil (Egloff & Nelson, 1933). The company objective was to find an alternative for petroleum fuel production. The process was the same applied on petroleum cracking in that time, with temperature range of 718-758 K and at 931.36 kPa. The product was distilled. The result was organic compounds with boiling point on gasoline rage, 57.8% for cottonseed oil and 59.9% for seal oil. The gaseous product was composed of: light hydrocarbons, carbon oxides, water and nitrogen.

The main objective was apply pyrolysis for an improvement of natural oils to use on internal combustion engines. With the evolution of analytical technics and better understanding of oil composition, the scientific community looked for the pyrolysis of model molecules, to improve the understanding on oil pyrolysis. The vegetable oil was mainly composed by triglycerides, and its respective fatty acids associated with glycerol, each one of these was studied separately to understand the mechanism of process.

Works involving pyrolysis of fatty acids [oleic acid (Asomaning, Mussone, & Bressler, 2014b), stearic acid (K. D. Maher, Kirkwood, Gray, & Bressler, 2008)) and triglycerides model molecules (trilaurin(Kitamura, 1971), tristearin (Higman, Schmeltz, Higman, &

Chortyk, 1973), tripalmitin (Higman et al., 1973; Kitamura, 1971)], are executed experimentally and by simulation under force camp, via ReaxFF(Z. Zhang, Yan, & Zhang, 2013).

PYROLYSIS OF MODEL MOLECULES

This section involves the discussion of pyrolysis on vegetable oils model molecules and the reaction mechanisms proposed, giving focus for the major advances. Pyrolysis of fatty acids as molecules models was performed by various actors (Table 1), among other reasons to understand the process of fragmentation and deoxygenation of acids that compose triglycerides of oils and fats.

Table 1 - Studies of model molecules pyrolysis

Raw material	Reactor	Temperature [°C]	Way	Time [h]	Ref.
Oleic Acid	Batch	350-450	N ₂	0.5-8.0	(Asomaning et al., 2014b)
Fatty Acids Poly -unsaturated.	Batch	350-450	N ₂	0.5-8.0	(Asomaning, Mussone, & Bressler, 2014a)
Stearic acid	Batch	350-450	N ₂	0.5-0.8	(K. D. Maher et al., 2008)
Trilaurin e tripalmitin	Semi-batch	400-600	N ₂	-	(Kitamura, 1971)
Tripalmitin e tristearin	Semi-batch	400	N ₂	-	(Higman et al., 1973)
Tripalmitin	Simulation	1227-1727	-	0 - 10 ⁻¹³	(Z. Zhang et al., 2013)

One of the main goals on pyrolysis of natural oil is the oxygen removal, which is heteroatom on oil composition and, as the sulfur and nitrogen on petroleum processing; their presence disrupts the storage and processing.

On evaluating the chain unsaturation on oleic and linoleic acid deoxygenating pyrolysis (Asomaning et al., 2014a, 2014b), deoxygenation by decarboxylation (DCX) and decarbonylation (DCN) was observed. For 4 h of reaction over 623-683 K, the DCN quantity exceeded DCX quantity and for higher temperatures the DCX quantity exceeded DCN. This increase was associated with gas-shift reaction, once for DCN occurrence the deoxygenation (DO) by reaction with H₂, which is produced by dehydrogenation (DH). Despite being part of the set of pyrolysis reactions, the hydrodeoxygenation (HDO) is not evident in the product description on this papers; the water found in the product is assigned to gas shift reactions and DCN.

Pyrolysis involves also fragmentation of carbon chains of fatty acids. For oleic acid (18:1) (Asomaning et al., 2014b), in low-temperature pyrolysis, the occurrence

of short chain acids in liquid product was observed, its amounts have decreased with reaction time increasing, as well with the increase in temperature of reaction. The presence of unsaturation has led to fragmentation of carbonic chain in carbons C₉ and C₁₀. That is evident by the presence of hydrocarbons with C₉ and C₁₀ carbons in its chains, and by the presence of acids with 9 and 10 carbons that fragmented without being deoxygenated, that added up to the other organic acids totaling 8.65% by weight of the total product.

On linoleic acid pyrolysis (18:2) (Asomaning et al., 2014a) whose unsaturation are in carbons 9 and 12, there was a similar fragmentation process. A fragmentation of carbonic chain in their unsaturation occurred. It was evidenced by the presence of hydrocarbons C₁ to C₄, where these hydrocarbons amount double in comparison with monounsaturated acids pyrolysis, both at 66 K and 4 h. This is by breaking the C=C bounds that are most unstable and are presents on chains at C₉ and C₁₂ carbons, if the fragmentation occurs, the product will be C₆ hydrocarbons, which can lead to breakage of the second unsaturation generating hydrocarbons C₄ or

smaller. When pyrolysis occurs with a saturated fatty acid as oleic acid (K. D. Maher et al., 2008), the behavior is similar, but it is clear that the stability of the oleic acid is much higher. At 663 K and 4 h of reaction, in batch reactor, a few short-chain hydrocarbons are found and smaller is the amount of short-chain organic acids.

Pyrolysis of unsaturated acids shows that the DO occurs at the same time that carbon chains fragmentation process. It is different from the pyrolysis of a saturated acid (K. D. Maher et al., 2008), where the DO process takes place primarily to fragmentation process, for unsaturated acids (Asomaning et al., 2014a, 2014b). In a way that facilitates DO process which occurs primarily by the difference of polarity in carbon chain. The longer is the chain of acid the harder is your deoxygenation. This is evident when we look at the amount of free acids in the final product over time for a given temperature. In the case of monounsaturated acid 16:1 (Asomaning et al., 2014b) after 4 h of reaction to 663 K, the total amount of acids in the final product is 8,65%, and for the poly-unsaturated acid 16:2 (Asomaning et al., 2014a) the amount for the same condition was 8,86%. That is very different from that produced saturated acid 18:0 (K. D. Maher et al., 2008) under the same conditions where, despite not reveal the value, is evident in your chromatogram after 4 h of reaction to 663 K there is still a lot of stearic acid from feed.

Variation of conditions in process modified products on similar way, regardless of the amount of unsaturation of raw material. Thus, on pyrolysis of free acids (Asomaning et al., 2014a, 2014b; K. D. Maher et al., 2008) the increase on reaction time favored hydrocarbons formation, occurred mainly through deoxygenation by loss of carbon oxides. The temperature increase associated with the increased of reaction time, increased cyclical chains content, as well as aromatic compounds, on product. Aromatic formation, directly linked to dehydrogenation, occurred mainly at higher temperatures, however for unsaturated reactant, part of this hydrogen was consumed by hydrogenation reactions, generating saturated hydrocarbons and acids.

In addition to free fatty acids thermal cracking, it is necessary to understand the behavior of pyrolysis when the process involves a triglyceride. For this, it was studied synthetic triglycerides Trilaurin (Kitamura, 1971) tripalmitin (Higman et al., 1973; Kitamura, 1971) and triestearin (Higman et al., 1973), under pyrolysis conditions. The product presented a large quantity of acids and some liquid hydrocarbon. By the nature of the semi-batch process, the saturation of acids

influenced the low quantities of hydrocarbons, there is no gas production. It was observed that there are large quantities of free acids and there were not from triglycerides, which may have been fragmented by the low pressure.

In addition to the experimental work the tripalmitin, it was studied by simulation of field in Reax FF, supported by the theories of quantum chemistry. The process involves a fast pyrolysis at 1227 °C and 1727 °C, where the exposure time is about some picoseconds. The simulation revealed that the breakdown of triglyceride is fast and occurs by central acid loss, followed by one of the other two acids loss. That ends up losing the radical by the formation of a double bond of glyceride connected to the last acid. This in turn gets separated from glyceride, generating a C₃ hydrocarbon with radical and the last free fatty acid. Then occur deoxygenation by decarboxylation of the free acids. The author does not address directly dehydrogenation reactions, but it shows a radical formation reactions leading to the formation of cyclic compounds. As triglycerides models with unsaturated fatty acids have not been tested by pyrolysis in a mechanism study, it is a risk to say that the breakdown of triglyceride will be the primary reaction process, without prior fragmentation of unsaturation was been noted when these are present (Asomaning et al., 2014a, 2014b).

The mechanisms for the molecules models of free acids and triglycerides, are also recorded in cracking of vegetable oils with different blends of free acids and triglycerides. The following section discusses the cracking of oils and brings the results and proposed mechanisms.

PYROLYSIS OF FATS AND OILS

Pyrolysis of organic oils and fats was studied using several factors, operational conditions, reactors and raw materials. The Table 2 brings a classification of the major selected works.

A wide variety of oils was submitted to pyrolysis, soybean (Kubátová et al., 2011; Lima et al., 2004; Zámotný, Bělohav, & Šmidrkal, 2012), canola (Idem, Katikaneni, & Bakhshi, 1996; Kubátová et al., 2011; Sadrameli & Green, 2007), palm (Lima et al., 2004; Zámotný et al., 2012), sunflower (Chen, Wang, Lu, & Yang, 2010) and rapeseed (Zámotný et al., 2012). Through the Table 2, the saturation of these oils It is clear and reveals that the vast majority of used oils

have high quantity of unsaturation, except the palm oil of Lima *et al.* (Lima *et al.*, 2004), which is composed mainly of saturated palmitic acid with many unsaturated acids. Such features of acids, as found by Asomaning *et al.* (Asomaning *et al.*, 2014a, 2014b), can influence the fragmentation of carbon chains.

The reactors used include micro pyrolysis reactor (MPR) semi-batch (Zámstný *et al.*, 2012), continuous fixed bed reactor (FBR) (Idem *et al.*, 1996), stirred batch reactor (SBR) (Biswas & Sharma, 2013; Kubátová *et al.*, 2011), batch reactor (BR) (Chen *et al.*, 2010), reaction

system and separation with recycle for a tubular reactor (RTR) (Sadrameli & Green, 2007), semi-batch reactor by distillation (DS-BR) (Lima *et al.*, 2004). For reactors with fixed beds it is common find the value of hourly space velocity, indicating the relationship between the of reagent flow and bed amount, giving an idea the time that the oil will be subject to the reactional conditions. In addition, some experimental procedures did not specify inert atmosphere but not specified if it was only reagent, thus, it is assumed that the atmosphere in the reactor is only reagent (R).

Table 2 – Non catalytic pyrolysis of vegetable oil

Oil used	Carbon number: unsat (%)	Reactor	Way	Temperature [°C]	Pressure [kPa]	Time [h]	Analyses	Ref.
Canola	18:1(60);18:2(20); 18:3(10)	RTR	-	300-500	101.33	5-24.2 ^c	CG-MS	(Sadrameli & Green, 2007)
Canola	18:1(60);18:2(20); 18:3(10)	SBR	N ₂	420-430	37232	0.16-0.33	CG-FIDMS	(Kubátová <i>et al.</i> , 2011)
Canola and steam H ₂ O	18:1(60);18:2(20); 18:3(10)	FBR	N ₂	300-500	101.33	3.3-640 ^A	CG-MS	(Idem <i>et al.</i> , 1996)
Colza high Erucic	22:1(48);18:1(17); 18:2(15)	MPR	N ₂	820	101,33	8.3*10 ⁻⁵	CG-MS	(Zámstný <i>et al.</i> , 2012)
Colza Low Erucic	18:1(59);18:2(23);21:0(5)	MPR	N ₂	820	101,33	8.3*10 ⁻⁵	CG-MS	(Zámstný <i>et al.</i> , 2012)
Sunflower	18:2(66);18:1(27);18:0(2,8)	BR	R	400	18000	0.33	CG-MS/EB	(Chen <i>et al.</i> , 2010)
Castor bean	18:1:OH (88) Ricinoleico	DS-BR	R	350-400	101,33	-	CG-MS- FTIR-LIQ	(Lima <i>et al.</i> , 2004)
Palma	18:1(44);16:0(35);18:2(12)	MPR	N ₂	820	101,33	8.3*10 ⁻⁵	CG-MS	(Zámstný <i>et al.</i> , 2012)
Palma	16:0(35);18:1(44);18:2(15)	DS-BR	R	350-400	101,33	-	CG-MS-FTIR	(Lima <i>et al.</i> , 2004)
Soybean	18:2(51);18:1(24);16:0(11)	MPR	N ₂	820	101,33	8.3*10 ⁻⁵	CG-MS	(Zámstný <i>et al.</i> , 2012)
Soybean	18:2(43);18:1(25);18:0(11)	SBR	N ₂	420-430	37232	0.16-0.33	CG-FIDMS	(Kubátová <i>et al.</i> , 2011)
Soybean	18:2(52);18:1(24);16:0(14)	DS-BR	R	350-400	101,33	-	CG-MS-FTIR	(Lima <i>et al.</i> , 2004)
Rapeseed	-	SBR	N ₂	460-500	101,33	0.17	ATG, CG-MS	(Biswas & Sharma, 2013)

^A - Gas hourly space velocity (GHSV); ^B Elemental Analysis; ^C - Mass flow rate (g/h)

Temperatures on the selected works (Table 2) range from 300 to 800 °C, focusing the moderate temperatures of 400 °C. The pressure used in these works depends on reactor type. In general those who operate in Batch, the pyrolysis occurs over time, generate gas and the pressure increases, varying over time, reaching a maximum shown in the Table 2.

The analysis of the products is also quite relevant, when improving the quality of oil for use in internal combustion engines is desired. The best way to evaluate this improvement is quantifying the oxygenated compounds in the final product, because these give undesirable characteristics as low freezing point, acidity, storage issues, among others. The selected works have

analyzed the products by gas chromatography coupled to mass spectrometry, allowing a quantification and identification of oxygenated compounds. Only Chen *et al.* (Chen *et al.*, 2010) assess elemental analysis for product composition. The only technique employed able to evaluate the presence of oil triglycerides in the final product was presented by Lima *et al.* (Lima *et al.*, 2004), using FTIR to evaluate the links and qualify the presence of Triglycerides.

With a complex composition, it is interesting to split the discussion of the products of pyrolysis for its phase. Therefore, gaseous products are compared, liquid and solid products in the following sections.

GASEOUS PRODUCTS

The gas phase of the products is evident when it comes to continuous tubular reactors and Batch reactors. For the semi-Batch, the liquids out of the reactor in the gas phase, but they were separated from the gases by cooling. Thus, the gaseous products at room temperature were considered. The profile of these products is qualitatively similar in all papers evaluated, being composed of carbon oxides, hydrogen, water and light hydrocarbons (C₁-C₅), saturated or not.

In the pyrolysis of sunflower oil, Chen *et al.* (Chen *et al.*, 2010) evaluated the gaseous product and determines that 6.4% the oil was converted into gas and the most abundant compound in this phase is the carbon dioxide, 3.8% and carbon monoxide, 1.07%, with 0.17% saturated hydrocarbons and 1.38% of unsaturated, with only traces of hydrogen. These results indicate that the combination of reactor and a low reaction time was not effective in fragmentation of molecules, by low production of hydrocarbons. However it was obtained a good amount of carbon oxides, showing a good deoxygenation. For example, at the same temperature, 400°C, pyrolysis of canola oil (Sadrameli & Green, 2007) converted 55.5% of oil in gas, with the composition of 23.4% of saturated hydrocarbons and 28.1% of unsaturated, with 2.9% of carbon oxides and 0.9% of hydrogen, a similar result to the same oil was reported by Idem *et al.* (Idem *et al.*, 1996). Despite having produced less CO_x, the amount of hydrocarbons in the gaseous product is much larger, what could be attributed to the reactor used.

Pyrolysis of sunflower oil was performed in Batch reactor, where the pressure increases over time, causing the oil saturation, and although sunflower oil be more poly-unsaturated, it was not be fragmented into Batch. However in a continuous reactor, with room for the

expansion of gases, the hydrogen produced remained in the gas phase, without hydrogenate the oil and, in this way, unsaturation could be fragmented without necessarily the deoxygenation occur, generating more hydrocarbons in gas phase, as predicted by the model molecule tests (Asomaning *et al.*, 2014a).

In a Batch reactor pyrolysis of canola and soy oil were realized (Kubátová *et al.*, 2011), however for the gaseous product discussion, there was no quantification of carbon oxides, specifying only hydrocarbons. Although soybean oil have more than double of unsaturation in its acids that the canola oil, not noted significant difference in the composition of gaseous hydrocarbons of the two processes.

On fast pyrolysis (Zámotný *et al.*, 2012), soybean, palm and rapeseed oils were processed with a residence time of 0.3 s, and a temperature of 820 °C. On these reactional conditions, the conversion was 99% where all the oxygen of oils has been released in the form of carbon dioxide. In this research the relationship of the products with the amount of unsaturation of acids of oils was emphasized. With the increase in the number of unsaturation it was observed a reduction in the amount of ethylene and propylene in the gas phase, indicating that saturated oil would produce a greater fraction of these products.

Another very important molecule in the gaseous product in that process is the propylene and propane. These are a direct indicator of decomposition of glycerides, being present, in varying amounts, in all products of pyrolysis of the evaluated works. However not all the molecules of these compounds comes from the decomposition of just triglyceride and not all molecules of CH₂=CH-CH* are hydrogenated to propane and propylene, and may be undergo a reaction if oligomerization (Z. Zhang *et al.*, 2013).

LIQUID PRODUCTS

The liquid product of pyrolysis of triglycerides involves several compounds. There are: not decomposed triglyceride; free fatty acids, produced from triglycerides; free acids arising from fragmentation; saturated hydrocarbons; cyclic unsaturated hydrocarbon; aromatic, and water for some cases.

Comparing again the works, in the pyrolysis of sunflower oil, Chen *et al.* (Chen *et al.*, 2010) evaluates the liquid products presented. It was composed by: 15.73% of saturated hydrocarbons; 22.6% of unsaturated hydrocarbons; 2.76% of aromatics; 13.75% carbonilated compounds; 5.48% of fragmented acids and 32.6% of

acids from oil, in molar percent. The elemental analysis revealed that 7.47% of the final product is oxygen in mass percent, noting that there is no nitrogen and the ratio H/C is 1.95, indicating a dehydrogenated product. Comparing with pyrolysis of canola oil at the same temperature (Sadrameli & Green, 2007), it was obtained a quantity of aromatic hydrocarbons 13.5% and linear of 1.5%, being 18% liquid product unidentified assigned to triglycerides and free acids. At this point it is interesting to make a parallel with the result (aromatic hydrocarbons) obtained by Zámotný *et al.* (2012), using different oils. It was observed that with the increase of the unsaturation number of oil, there was an increase in the aromatic hydrocarbon amount on final product. The sunflower oil has double of unsaturation that the canola oil and produced less aromatic than this. This difference can be attributed to reactor used, where the sunflower pyrolysis occurred in a Batch system closed and the hydrogen produced saturate carbon chains, being consumed during the reaction. For a flow system using canola oil, which is more saturated, there was no production of hydrogen thus there was producing more aromatic hydrocarbons. On the other hand, in a Batch reactor the oil will be saturated by action of the pressure generated in the process, while for the system in flux, the pressure is not enough to make it happen, unless it is pressurized.

There was no significant difference between the Batch pyrolysis of canola and soybean oils (Kubátová *et al.*, 2011) considering gaseous products but in the liquid product the difference is clear. The canola oil pyrolysis liquid product had 39.4% of saturated hydrocarbons and 11.2% of unsaturated, with 7.2% aromatic, 0.4% carbonilated compounds and 15.3% of acids, being 13.4% fragmented acids. For soybean oil, under the same conditions, it was obtained 36.2% of saturated hydrocarbons and 11.7% of unsaturated, with 7.5% of aromatics, 0.4% of carbonilated compounds and 27.1% of acids, being 25% of fragmented acids. The more significant difference is the amount of acid in the product, the canola oil is more unsaturated than soybean oil, and this facilitated his deoxygenation, for the least amount of acids in the product. As expected the deoxygenation is facilitated for the unsaturated and polyunsaturated acids (Asomaning *et al.*, 2014a, 2014b).

When evaluating the results, it is observed that there are two crucial factors for the pyrolysis of triglycerides. First the oil saturation influences directly in the process, whenever it was evaluated for the molecules models or for oils. It was observed that a greater unsaturation facilitates fragmentation and the deoxygenation, which is interesting when you want gaseous and light liquid hydrocarbons, but when the goal is the production of

diesel, fragmentation is not required, much less aromatic formation, which is also improved by the presence of unsaturation. The second factor is the reactor used, basically the pressure involved in the process. It is important even for less saturated oils. The pressure limits the aromatic and light hydrocarbon. When the reactor is less pressured, less of these compounds were produced, which is good if you want to produce hydrocarbons like diesel.

The results show in practice the possibility of deoxygenating vegetable oils without a catalyst. However the products generated by the pyrolysis of these oils require a separation step by the presence of undesired free acids, which need another pyrolysis (Sadrameli & Green, 2007). With a selective catalyst for a particular reaction it is possible to achieve a significant improvement in the quality of the products in deoxygenation and fragmentation parameters. The next section deals with catalytic cracking, which involves catalysts with this goal.

1.1 CATALYTIC PROCESSING

As well as pyrolysis, catalytic cracking of vegetable oils is a process that involves high temperatures and pressures, which leads to fragmentation of fatty acids and its reductions by different pathways reactions. The purpose of using a catalyst is to make a selective process for desired reactions, as well as to accelerate them in order to occur in mild operation conditions.

Several papers related to scientific literature focus on catalytic processing of oil raw materials, where the most recent ones use catalysts for cracking and hydroprocess (Satyarthi *et al.*, 2013) and they also explore the use of different catalysts in order to obtain biofuels like gasoline or diesel.

This section aims to address aspects of catalytic cracking and deoxygenation of vegetable oils, as well as to highlight the most relevant results of some outstanding work in the use of these technologies.

CRACKING AND DEOXYGENATION OF MOLECULES MODELS

As well as the pyrolysis of oils, various researches involve the observation of molecule models in order to have greater control over the variables included and thus understand the reaction mechanisms, the Table 3 shows a general summary of the research using molecules models for this objective.

Table 3 - catalytic Processing of model molecules

Catalyst	Molecule	Process	Reactor	Way	Temperature [°C]	Pressure [MPa]	Time	Ref.
Na, H-ZSM-5	Myristic acid 14:0	Crack	MPR	He	650	-	35 s	(Fréty et al., 2014)
NiMo/ SAPO-5	Oleic Acid	Crack	MPR	He	650	-	35 s	(Fréty et al., 2014)
SAPO-5	Oleic Acid	Crack	MPR	He	650	-	35 s	(Fréty et al., 2014)
Pt/ SAPO-11	Oleic Acid	DOX	SBR	CO ₂ H ₂	200-325	2	0.16-2 h	(Ahmadi, Macias, Jasinski, Ratnasamy, & Carreon, 2014)
Pt/Al ₂ O ₃	Oleic Acid	DOX	SBR	CO ₂ H ₂	200-325	2	0.16-2 h	(Ahmadi et al., 2014)
NiW/ SiO ₂ Al ₂ O ₃ NTY zeolite	Stearic, oleic and Linoleic-mixing	DOX	FBR	H ₂	300-375	2-8	4-6 h ⁻¹	(Yang, Wang, Zhang, Wang, & Li, 2013)
Ni, Pt, Pd, and Co/ γ -Al ₂ O ₃	Oleic Acid	DOX	FBR	H ₂ , N ₂	330	5	1h ⁻¹	(Srija, Faungnawakij, Itthibenchapong, 2014)
Ni, Mo, NiMo /HY	n-Decane	Crack	FBR	H ₂	325	3	1-12 h	(Egia et al., 1998)
Pd/C	Oleic, linoleic and stearic acid	DOX	PBR	He, H ₂	300	1.5	0-5h	(Immer, Kelly, & Lamb, 2010)
Ni/C; Pd/C; Pt/C	tristearin, triolein and soybean oil	DOX-Crack	Batch	H ₂	350	0.7	1-4h	(Morgan, Grubb, Santillan-Jimenez, 2010)

(a) Weight hourly space velocity (b) Semi-bath with gas flow reactor

The materials used are divided in two categories: unsupported catalyst and metals supported on a low acidity support. The catalytic characteristics have influence directly on the process, indicating what pathway reactions will occur preferentially (Sankaranarayanan, Banu, Pandurangan, & Sivasanker, 2011). When the acidity of the catalyst is high, it usually causes cracking of the molecules due to acceleration of fission reactions of C-C bonds. However, when the catalyst is a supported metal, generally the deoxygenation reactions (DO) are accelerated.

In the cracking of myristic acid using NaZSM5 and HZSM-5 catalyst (Fréty et al., 2014), the compounds produced with chain of C₃-C₁₃ were evaluated. There was a big difference between the two catalysts, where the conversion was 15% higher than the amount of oxygenated compounds, which was 2.2% lower for HZSM5, producing twice the hydrocarbon than NaZSM-5. The amount of mono and poly aromatic hydrocarbons was much greater for HZSM-5 catalyst, due to a preference for dehydrogenation in the process.

The hydroprocessing of the oleic acid using SAPO-5 and NiMo/SAPO-5 catalyst (Fréty et al., 2014) had a big difference in cracking products distribution. The liquid

product using SAPO-5 catalyst was rich in unsaturated hydrocarbons (66%) and aromatics (38%). This result is expected for acid support, which increase the dehydrogenation reactions rate, with 2.1% and 7.3% of alcoholic organic acids, thus obtaining a high degree of deoxygenation. With the metal catalyst, 48% of saturated hydrocarbons without any aromatic hydrocarbon were obtained, indicating the effect of the presence of nickel as hydrogenating agent, once saturated cyclic hydrocarbons (3%) was produced. The difference of the amount of aldehydes (37.7%) and alcohol (2.1%) in the product suggests that hydrogenation from the metal sites inhibited mainly the full deoxygenation of acid by the reaction of -OH with hydrogen, forming aldehydes, but also to attack with less intensity the =O bonds forming alcohol. Moreover, Egia et al. (Egia et al., 1998) employed n-Decane like model molecule at variable temperature and pressure. Under these conditions, it was found that there is no relationship between the degree of saturation of products and the degree of acidity of the catalyst. Another important conclusion of this work is that for both catalysts were obtained unsaturated hydrocarbons, usually linear by breaking the double bond in the reactions of DCN and DCX, as found by Asomaning et al. (Asomaning et al., 2014a, 2014b).

As observed in pyrolysis experiments in batch reactors hydrogenation reactions (HDG) are favored (Chen et al., 2010) and as a consequence less aromatics are formed. For the same type of reactor using supported platinum catalysts, oleic acid has been deoxygenated under atmosphere of H_2 and CO_2 (Ahmadi et al., 2014). By varying the temperature of 200 to 350 °C in 2h of reaction on Pt/SAPO-11, it was found that conversion of hydrocarbons increased with temperature under reduced conditions, reaching 98% at 350 °C, where hydrocarbons produced were mostly linear with 21% of aromatics. The increased temperature did not affect significantly the fragmentation of chains, but favored hydrogenation once it produced 43% of aromatics to 200 °C, favoring also the selectivity to heptadecane that rose from 8% in the product (200 °C) to 32% (350 °C).

Using Pt/SAPO-11 catalyst and in presence of hydrogen (Ahmadi et al., 2014), at 350 °C, it was found that the conversion of acids and heptadecane selectivity increased, as well as the concentration of aromatics decreased, without modifying significantly the amount of hydrocarbons. The results were attributed to the HDG reactions of oleic acid, by its conversion to stearic acid, also present in products. This conversion improved improving the stability of carbonic chain, decreasing the amount of fragmentation, since the presence of unsaturation facilitates the breakdown (Asomaning et al., 2014b), reducing the size of the carbonic chain of products. The presence of the catalyst improved significantly the reaction. Deoxygenation at 350 °C in 0.5 h of reaction product contained only 2.3% of organic acids in presence of H_2 and 5.5% in presence of CO_2 . For oleic acid, pyrolysis at 390 °C and 1h of reaction in a batch reactor, with N_2 , generated an amount of 40% of organic acids on the product. Likewise, Immer et al (Immer et al., 2010) found in the catalytic cracking of stearic, oleic and linoleic acid using Pd/C catalyst, where the reactions of HDG with H_2 present higher yield of n-heptadecane (98% of liquid product) than with inert (He).

The effect of CO_2 was not positive for the deoxygenation of stearic acid on Pt/SAPO-11 (Ahmadi et al., 2014). At the best condition of reaction (350 °C and 2h), the conversion was 94.5% and selectivity 21.8% for heptadecane. The quantity of hydrocarbons was higher than reducing conditions. This result indicates that there was cracking of unsaturated chains, which have not been saturated because they were not on reducing conditions. The temperature and time had similar effects to the two conditions, increasing the conversion of acids and the selectivity to hydrocarbons.

Oleic acid was treated using Pt/SAPO-5 and Pt/ Al_2O_3 catalyst (Ahmadi et al., 2014), in a batch reactor at 325 °C and 300 °C, respectively, with H_2 and 2 h to compare the support. Selectivity of SAPO-11 for heptadecane was the lowest (32%) due to the acidity of the material, which promotes dehydrogenation reactions. Selectivity of Al_2O_3 for heptadecane was significant (63%) indicating that the material support can promotes deoxygenation cracking. This result shows the support effect to promote certain pathway reaction for cracking. Acid support would be idea, if the objective to produce light hydrocarbons, 1, whereas if the purpose is the diesel, a neutral or slightly acid support would lead to good results.

The effect of hydroprocess of a mixture of fatty acids (5% stearic, 77% oleic, 18% linoleic) solubilized in dodecane, was evaluated in a continuous fixed bed reactor over NiW/ $SiO_2-Al_2O_3$ catalyst (7.5 g) (Yang et al., 2013). The first assessment to 20 wt.% of acids in dodecane to 1 g/min, the activity remained was closed to 100% for 60 h of reaction, 350 °C and 5 MPa of H_2 (450 mL/min). The material was selective to HDO compared to DCN and DCX due to the product presented higher composition of hydrocarbons C_{18} and C_{16} than C_{17} and C_{15} .

The temperature effect was positive in relation to conversion when was compared to the same conditions (1 g/min of the solution and 225 mL/min of H_2) for hydrotreating using NiW/ $SiO_2-Al_2O_3$ catalyst (Yang et al., 2013) The conversion was nearly complete at 300 °C with a large amount of C_{18} product. However, the increase in temperature failed to reach 100% conversion but decreased the content of long-chain hydrocarbons C_{18} . Therefore, selectivity to octadecane (C_{18}) decreased with temperature increase. Pressure effect at 350 °C, reversed the relationship C_{18}/C_{17} . At 2 MPa, the quantity of C_{18} was higher than C_{17} . It was reversed when the pressure increase to 5 MPa and it was intensified at 8 MPa. This effect was attributed to the increase of acids in HDO. However for the same slight variation decreased C_{15} and C_{16} hydrocarbons quantities. It was due to increasing temperature, support proposal α and β bonds reactions scission, where the oleic acid, hydrogenated, form C_{15} hydrocarbon after α -scission and C_{16} after β -scission, with acetic and propionic acids, respectively.

The mechanism of the reaction was evaluated by the use of oleic acid as model molecule (Srifa et al., 2014). The results led the proposition of the mechanism that involves the reactions of HDO, DCN, DCX, HDG, Esterification and hydrogenolysis. As result of the reaction was

obtained several oxygenated intermediates as acids, alcohols and esters, but did not obtained aldehyde. These compounds come from incomplete DOX. Was the metal that had the best performance, as well as the only one who presented HDO. The conversion of other metals Pt, Pd and Ni were also complete, however the main mechanism of deoxygenation was loss of carbon oxides.

DEOXYGENATION OF VEGETABLE OIL

Different types of catalysts have been used in the process of vegetable oils. A summary of some of the studies found in the scientific literature is presented in the Table 4. All works were made by analyzing the most significant reaction variables: type of oil, reactor, temperature, pressure and reaction time, as well as its effect on the production of biofuel.

Table 4 Catalyst for deoxygenation of vegetable oils

Catalyst	Oil	Process	Reactor	Way	Temperature [°C]	Pressure [MPa]	Time	Ref.
Ni/SiO ₂ Ni-Mo/ γ -Al ₂ O ₃	Babassu, Soybean	DOX	Batch	H ₂	370-400	15-30	2h	(Gusmão et al., 1989)
NiMoCe/ Al ₂ O ₃ ; NiMoLa/ Al ₂ O ₃	Jatropha	DOX	FBR	H ₂	370	3.5	0.9 h ^{-1*}	(J. Liu, Fan, Tian, Liu, & Rong, 2012)
NiMo/Al ₂ O ₃ Pd/C	Palm	DOX	Semi-Batch	H ₂	350-450	2-6	3h	(Kiatkittipong et al., 2013)
NiMo/ Al ₂ O ₃	Rapeseed	DOX	LFR	H ₂	310-360	7-15	1h ^{-1**}	(Šimáček, Kubička, Šebor, & Pospíšil, 2010)
NiMo/ Al ₂ O ₃	Rapeseed	DOX	LFR	H ₂	260-340	7	1h	(Šimáček, Kubička, Šebor, & Pospíšil, 2009)
NiMo, PtPd/Al ₂ O ₃	Jatropha	DOX	FBR	H ₂	330-390	3	2 h ^{-1*}	(Gong, Shinozaki, Shi, & Qian, 2012)
NiMoS massic	Waste	DOX	Batch	H ₂	300-375	9	2h	(H. Zhang, Lin, Wang, Zheng, & Hu, 2014)
NiMo/Al ₂ O ₃	Gasoil-Palma Mixtures	DOX	TBR	H ₂	310-350	3.3	0.5-2.5 h ^{-1**}	(Vonortas, Kubička, & Papayannakos, 2014)
CoMo/ γ -Al ₂ O ₃	Gasoil-Palma Mixtures	DOX	TBR	H ₂	310-350	3.3	0.7-1.4 h ^{-1**}	(Templis, Vonortas, Sebos, & Papayannakos, 2011)
NiMo/Al ₂ O ₃ CoMo/Al ₂ O ₃	Gasoil-Waste oil	DOX	FBR	H ₂	330-370	5.5	1 h ^{-1*}	(Bezergianni, Dimitriadis, & Meletidis, 2014)
Ni, Pt, Pd and Co/ γ -Al ₂ O ₃	Palma	DOX	FBR	H ₂	330	5	1h ^{-1*}	(Sriřa et al., 2014)
Ni, Mo, Ni-Mo/ Al ₂ O ₃	Colza	DOX	FBR	H ₂	260-380	3.5	0,25-4 h ^{-1**}	(Kubička & Kaluža, 2010)
NiO-MoO ₃ - γ -Al ₂ O ₃ / β -Zeolite	Gasoil-Sunflower	DOX	FBR	H ₂	320-350	3-6	1-4h ^{-1*}	(Sankaranarayanan et al., 2011)
Ni ₂ P/ Silica; Ni ₂ P/HY	Soybean	DOX	TBR	H ₂	340-370	3	1-3h ^{-1*}	(Zarchin, Rabaev, Vidruk-Nehemya, Landau, & Herskowitz, 2015)
CoMo, NiMo/Al ₂ O ₃	Jatropha cruces	DOX	CFTR	H ₂	310-390	2.8	15.2h ^{-1*}	(García-Dávila et al., 2014)intermediates and final compounds
CoMo/Al ₂ O ₃	Sunflower	DOX	FBR	H ₂	380	4-8	1 h ^{-1*}	(Krár, Kovács, Kalló, & Hancsók, 2010)
Ni/ZSM5	Castor	DOX	FBR	H ₂	300	3	2 h ^{-1**}	(S. Liu, Zhu, Guan, He, & Li, 2015)
Ni ₂ P/SAPO-11; Ni/ MCM-41	Castor	DOX	FBR	H ₂	300	3	2 h ^{-1**}	(S. Liu et al., 2015)
NiMo/ γ -Al ₂ O ₃	Soybean	DOX	Batch	H ₂	400	9.2	1h	(Veriansyah et al., 2012)
Pd; CoMo; Ni/ SiO ₂ ; Pt; Ru/ γ -Al ₂ O ₃	Soybean	DOX	Batch	H ₂	400	9.2	1h	(Veriansyah et al., 2012)

*LHSV – Liquid Hourly Space Velocity – (Reactant Liquid Flow Rate)/(Reactor Volume)

**WHSV - Weight Hourly Space Velocity – (Mass Flow)/(Catalyst Mass)

Hydrotreatment of soybean oil and babassu oil using Ni/SiO₂ catalyst in a batch reactor with H₂ pressurized was made by Gusmão et al.(1989). Hydrogenation of unsaturated acids was observed due to pressure loss at 190 °C. In this study, hydrogen consumption favors the production of long-chain hydrocarbons due to the cracking of saturated bonds is more difficult than the unsaturated. Moreover, the reaction products were mainly C₁₁ and C₁₂ for the babassu oil whereas for soybean oil was C₁₇ and C₁₈ due to low acidity of support (SiO₂) and metal (Ni). This mixture is characteristic of oil cracked without previous deoxygenation. Furthermore, pressure-increasing make decreased thermodynamically of breaking carbons bonds. A small increase in temperature hydrogenation of soybean oil using NiMo/γ-Al₂O₃ catalyst was presented, which occurred between 225 and 280 °C, without others changes in triglyceride degradation temperature at 360 °C, this represented an advantage due to traces of sulfur poisoning Ni sites at this temperature.

Hydroprocess of rapeseed oil at variable temperature (260-340°C) and 7 Mpa using NiMo/ γ-Al₂O₃ catalyst was made for Simacek et al (Šimáček et al., 2009), they was obtained mostly hydrocarbons type C₁₇-C₁₈ due to that metal properties of NiMo that favored the HDO of vegetable oil. Afterwards, in later study (Šimáček et al., 2010) physical-chemical properties such as density, cetane number and nitrogen number was availed. They used different mixtures of gasoil:liquid product of reaction (0-30 wt %), the values of these mixtures are accepted by international standards such EM-590. Gong et al. (Gong et al., 2012) studied hydrotreatment of Jatropha oil to 330-390°C and 3Mpa. They found that the liquid fraction of the product up to 82 wt% which have similar properties to those of diesel from petroleum. This study also corroborate with the influence made by combining Ni and Mo for the development of HDO as preferred reaction path. On the other hand, Kiatkittipong et al (Kiatkittipong et al., 2013) studied the effect of reaction time, temperature and pressure in the hydroprocess of crude and refined palm oil using NiMo/γ-Al₂O₃ catalyst, It was obtained 81% yields of hydrocarbons in the range of diesel at 375 °C and LHSV 0.5 h⁻¹.

Zhang et al.(H. Zhang et al., 2014) investigated the kinetics developed on HDO through the hydroprocess of cooking oil at temperatures between 300-375 °C and 9 MPa. It was explicated the oxygen elimination, since the transfer of fatty acids, firstly to aldehydes, them to

alcohols, and finally, to hydrocarbons. Also, was found that DCX and DCN eliminate more oxygen (up to three times more) than HDO.

The use of these catalysts has been extended to the hydroprocess of gasoil:vegetal oil mixture. Vonortas et al (Vonortas et al., 2014) mixed gasoil:Palm oil in different concentrations (5, 10, 15 and 30 wt% of oil) and treated it at variable temperature (310-350 °C) and 3.3 MPa. From the analysis of products, they found that the reaction pathways present were mostly HDC (55 wt% of the liquid fraction). Similarly, by a kinetic Study, it was found that the addition of vegetable oil could decrease the reaction rate of the Hydrodesulfurization (HDS) due to dilution made in the reactor inlet. Bezergianni et al (Bezergianni et al., 2014) compared the yield of NiMo and CoMo like active phases in hydroprocess of mixture gasoil:cooking oil at different concentrations (10 and 30 v/v%) with variable temperature (330-370°C) and 5.5 MPa. It was found that the quantities of oxygen removed in the reaction catalyzed by NiMo depended to initial concentration of gasoil:cooking oil; for example, in the composition of products found that the oxygen content increased from 0.38 wt% in a mix 90:10 to 1.51 wt% in a 70:30 mixture; However, the reaction catalyzed with CoMo was invariant.

Sankaranarayan et al (Sankaranarayanan et al., 2011) also studied co-process of gasoil:vegetal oil mixtures using NiO and MoO₃ supported in β-Zeolite, found that the addition of the β-Zeolite catalytic increased the conversion to 100% close to 330° C, compared to the 95% with NiMo/Alumina at the same temperature.

Liu *et al.* (J. Liu, Fan, et al., 2012) evaluated the performance of Ce and La in DOX of Jatropha oil in a fixed bed reactor under 3.5 MPa of H₂. Using NiMoLa/Al₂O₃ catalyst, with 5% of La, at 400 °C, the conversion overcame to catalyst without metal in 11%. In the catalyst NiMoCe/Al₂O₃, with 5% of Ce, to 400 °C, the conversion overcame the catalyzed reaction without metal in 13%. The sulfured catalyst NiMo/Al₂O₃ featured a higher performance at lower temperatures, having a conversion closed to 97% at 400° C, near to the tri-metallic catalysts and above that of non-sulfured bi-metallic catalyst. Incrementing of yield of long-chain hydrocarbons was observed when the concentration of Ce increases. Whereas for increasing La was a slight reduction in this selectivity. The long test time (180h) showed that the catalyst, after 100 h has stability with conversion of 70% for La and 80% for Ce.

DOX of palm oil performance was evaluated by Srifa et al. (Srifa et al., 2014) by using of different metals on gamma alumina for this, it was tested Ni, Pt, Pd and Co. Preliminary tests with the support showed very little catalytic activity for DOX reactions. Complete conversion of triglycerides was obtained only for metal concentrations higher of 2 wt%, and increasing of these metals made improved yield of products. The Co showed selectivity for HDO reaction (50%) but was also occurs DCN and DCX reactions to. For the other metals, these two reactions were prevalent in relation with HDO which occurring in small amounts that ranged from metal to metal. The main product of the reaction to Pt, Ni and Pd were the n-alkanes C_{15} and C_{17} , but for cobalt was the n-alkanes C_{15} , C_{16} , C_{17} and C_{18} , where the yield non-varied significantly from metal to metal. The main Gaseous products compose was methane, which was due to the methanation reactions of carbon oxides by the absence of these in the product, being the Co and Ni the more selective to CH_4 .

Also Kubicka et al. (Kubička & Kaluža, 2010) used Ni, Mo and NiMo supported on alumina to compare the effect of interaction of the bi-metallic catalysts on rapeseed oil in DOX. They found differences in the products distribution and the catalyst activity. The NiMo interaction for a specific temperature reached higher conversions (92%) than the only Ni (38%) or Mo (62%). NiMo catalyst at similar conversion had higher selectivity to larger hydrocarbons than Ni or Mo.

In addition to traditional transition metals Ni, Co and Mo, have been used nobles metals for DOX reactions. Veriansyah et al. (Veriansyah et al., 2012) studied the effect active phase variation in hydroprocess of soybean oil to 400 °C and 9.2 MPa. NiMo and CoMo bimetallic catalysts and Pd, Pt and Ru in $\gamma-Al_2O_3$ monometallic were used. The higher conversions were obtained with the NiMo (92.9%) and Pd (91.9%) and the hydrocarbons in the liquid phase were mainly C_{17} and C_{15} . According to the analysis of gaseous products it was able to determine that the NiMo favored the DCX and DCN reactions, while Pd and CoMo to HDO reaction. Moreover, it was observed isomerization of liquids using CoMo catalyst that as has been said, improves the properties of biofuel.

Using a neutral or slightly acid support, it could get diesel of high quality from vegetable oils with very low sulphur content. The long carbon chains form whole maintained by a combination of pressure, shifting

the balance, metal sites with hydrogenate capacity, promoting the saturation of double bonds and a holder with low acidity, not coming to break the links between carbons or dehydrogenating strings.

VEGETABLE OIL CRACKING

In addition to the catalytic DOX of acids of triglycerides, is common in this process occur fragmentation of carbon chains of organic molecules by temperature effects or presence of acid sites. As the light fuel has a higher market value, due to demand, and better application features, often the objective is to produce gasoline and jet fuel. Doing so can be a challenge in the absence of a suitable catalyst, as was seen in purely thermal pyrolysis and catalytic converters with deoxygenation does not or slightly acid.

The Table 5 displays a list of the works of hydrocracking catalyst which can distinguish the most relevant operation variables as well as the type of catalyst employe.

Zeolite has had important role in oil processing since their discovery. This material has served as catalyst, as well as mass support for metal sites in order to improve their performance and originated DOX. Currently it is evaluated the performance of zeolites in the co-processing (Abbasov et al., 2014; Biswas et al., 2014; Doronin et al., 2012; Šimáček & Kubička, 2010; Tiwari et al., 2011) of mixtures of vegetable oil:oil and direct processing (Buzetzki et al., 2011; Doronin et al., 2012; Dupain et al., 2007; Ishihara et al., 2014; Nam et al., 2011; Y. S. Ooi et al., 2004; Y.-S. Ooi et al., 2004; Twaiq, Mohamed, et al., 2003; Twaiq et al., 1999; Twaiq, Zabidi, et al., 2003).

The co-processing of vegetable oil and oil is currently employed, which have a benefit because not drastic changes it needed to use the infrastructure already available in the oil industry. A mixture 10 wt% cotton seed oil:gas oil of vacuum (Abbasov et al., 2014) in conditions of maximum conversion (500 °C) using halloysite catalyst was co-processed. It was obtained a decrease in reaction selectivity to hydrocarbons in the gasoline range. Pore size had influence on this result, because the halloysite has the bigger pore size. It is easier for larger molecules move into the structure of the material and achieves the most internal sites, converting more molecules.

Table 5 Process with different hydrocracking catalysts

Catalyst	Oil	Process	Reactor	Way	Temperature [°C]	Pressure [MPa]	Time	Ref.
Haloisita and Y zeolite	Cottonseed	Co-proc.	FBR	N ₂	480-540	-	0.5-21 h ⁻¹	(Abbasov et al., 2014)
FCC	Palm-VGO	Co-proc.	FBR	N ₂	450-530	-	30 s	(Doronin, Potapenko, & Sorokina, 2013)
NiMo/SiAl; ZSM-5-SiAl; ZSM-5 and FCC	Jatropha, VGO	Co-proc.	Batch	H ₂	450	0.101	0.4 h	(Biswas, Majhi, Mohanty, Pant, & Sharma, 2014)
NiMo/ Al ₂ O ₃	VGO-Rapeseed mixture	Co-proc.	PFR	H ₂	400-420	18	1 h ⁻¹	(Šimáček & Kubička, 2010)
sulfide Ni-W/SiO ₂ -Al ₂ O ₃	Soybean: refinery oil mixture	Co-proc.	FBR	H ₂	340-380	5	2.4 h ⁻¹	(Tiwari et al., 2011)
HZSM5, β-zeolite, USY	Palm	Crack	FBR	R	350-450	10 ⁻¹	1-4 h-1	(Twaiq, Zabidi, & Bhatia, 1999)
HZSM-5, HY, SiO ₂ , Al ₂ O ₃ , Al-Si and Montmorillonite	Coconut, Rapeseed Mustard, Sunflower	Crack	FBR	N ₂	450	-	30 s - 30 h ⁻¹	(Doronin, Potapenko, Lipin, Sorokina, & Buluchevskaya, 2012)
MC-SM-5/MCM-41	Vegetable oil Sludge	Crack	FBR	N ₂	480	-	12 h ⁻¹	(Nam et al., 2011)
USY, β-zeolite, HY, ZSM-5, Al ₂ O ₃	Soybean	Hydrocrack	FBR	H ₂	360	5	7 h ⁻¹	(Ishihara, Fukui, Nasu, & Hashimoto, 2014)
MCM41/ β-Zeolite	Palma Waste	Crack	FBR	N ₂	450	0.101	2.5 h ^{-1**}	(Y.-S. Ooi, Zakaria, Mohamed, & Bhatia, 2004)
MCM-41	Palm	Crack	FBR	N ₂	450	0.101	2.5 h ^{-1**}	(Twaiq, Zabidi, Mohamed, & Bhatia, 2003)
SiO ₂ -Al ₂ O ₃	Palm	Crack	FBR	N ₂	450	0.101	2.5 h ^{-1**}	(Twaiq, Mohamed, & Bhatia, 2003)
HZSM-5	Palm	Crack	FBR	N ₂	450	0.101	2.5 h ^{-1**}	(Y. S. Ooi, Zakaria, Mohamed, & Bhatia, 2004)
NaY, HY, HZSM-5	Rapeseed, Sunflower, Soybean and Jatropha	Crack	Batch	H ₂	350-440	3.5	0.5h	(Buzetzki, Sidorová, Cvengrošová, Kaszonyi, & Cvengroš, 2011)
FCC	Rapeseed	Crack	FBR	N ₂	485-585	-	2.5 h ^{-1**}	(Dupain, Costa, Schaverien, Makkee, & Moulijn, 2007)

**WHSV - Weight Hourly Space Velocity – (Mass Flow)/(Catalyst Mass)

The pore size effect in the cracking of palm oil is evident when comparing the products of process with zeolites of different sizes pores: ZSM-5 (0.54 x 0.56 nm), β -zeolites (0.56 x 0.74 nm) and USY (0.8 nm) (Twaiq et al., 1999). The distribution of products in the process had influence of temperature, surface mass speed and catalyst type. Varying the zeolite type, it was obtained the higher yield of diesel for USY, followed by β -zeolite and that less by ZSM5. These results suggest that zeolites with larger pores also promoted a lower production of gaseous hydrocarbons and gas. The temperature had a positive effect on conversion of palm oil triglycerides; its increase caused more fragmentation and higher selectivity to DOX reaction. Only the conversion of ZSM-5 had not influenced by temperature when the residence time was long. This material possesses high activity because it have greater acidity than other zeolites. The amount of gas obtained from cracking with acid catalysts is superior, due to fragmentation of the chains, and increasing temperature promotes further these fragmentations, for example, for the ZSM-5 at 400°C, the greatest gaseous product value of 47% composed mainly of hydrocarbons.

Commercially catalyst used for cracking in units of FCC (fluid catalytic cracking) is a mixture of materials, each one having a key role in the final catalyst activity. Doronin et al.(Doronin et al., 2012) evaluated the properties of two zeolite catalysts, HZSM-5 and HY with varied composition matrix Al_2O_3 , Si-Al rate and SiO_2 . It was studied cracking of sunflower oil using an mixture HY:HZSM-5 catalyst. The amount of gas produced was decreased whereas its hydrocarbon fraction increase when the amount of HZSM-5 rise. The activity of the matrix was well selectivity of gasoline with a lower gas production compared to the zeolites pure.

With a commercial FCC catalyst, the co-processing of sunflower oil with vacuum gas oil was valued (Doronin et al., 2013). For this catalyst, the result was different from the findings above (Abbasov et al., 2014). An improvement in the characteristics of the product with the addition of vegetable oil was found increasing the conversion and coke formed. The maximum selectivity of gasoline was increased introducing 5wt% of vegetable oil in the feed. However, its value varies with respect to the type of vegetable oil used. For example, at the same temperature, the selectivity of gasoline was 52.5% for sunflower oil and 50% for palm oil. This difference is due to the composition of oil triglycerides, where the sunflower oil is much more unsaturated than palm oil. Therefore, if the oil is more unsaturated, its gasoline selectivity and conversion will be higher. Its amount of

olefin and paraffin will be lower and its amount of mono and poly hydrocarbons and aromatics will be higher in the final product, like founded in the studies with model molecules.

Biswas et al.(Biswas et al., 2014) also investigated the performance of FCC catalyst and ZSM-5 in catalytic cracking of Jatropha oil, vacuum Gasoil and polyethylene blends. They found that the ZSM-5 provided the best activity to polyethylene:Jatropha oil blends cracking. It was found a liquid products fraction of 74 wt% of which 45wt% was hydrocarbons of gasoline range and 49wt% was hydrocarbons of the diesel range. For mixtures of vacuum Gasoil:Jatropha oil, it was obtain liquid fraction of 67wt%. Another interesting conclusion was that cracking made with ZSM-5 had positive effect on the pH value of the liquid fraction of the products.

The zeolites have typically micro-porous, selective to small molecules. Thus it is common in this process the search for mesoporous catalysts that can process larger molecules and produce less gas. When evaluating MC-ZSM -5/MCM-41(Nam et al., 2011), it was obtained a high conversion of glycerides of waste vegetable oil, where the main product was gasoline. About pyrolysis, the catalyst for increased conversion and reduced the formation of Coke, producing more gasoline and less kerosene, diesel and gaseous hydrocarbons. Therefore, this result suggests that the mesoporous structure improved selectivity to gasoline process.

CONCLUSION

When evaluating the possibilities of obtaining renewable fuels from vegetable oil with high temperature processing, it is possible to obtain high quality conventional fuels and less pollutants like sulfur and nitrogen. The characteristics of the equipment used, such as the type of flow and pressure, have key role in selectivity of the reactions that will occur in the process, where low pressure equipment tends to produce more gas than the pressurized.

Oil also represents a key role in the type of product you want to obtain. The higher the unsaturation of the oil the higher the fragmentation of carbon chains of acids from triglycerides and more selective the process will be to light hydrocarbons, but this can be reversed with the use of catalysts with high pressure of H_2 . The size of the carbon chains that comprise the triglycerides of oils also influences the product, once the little deoxygenation or cracking oligomerization runs; the greater will be the hydrocarbon chain of carbonic acid size of vegetable oil.

As the goal is to produce a fuel as an energy source and store this energy, it is important that the process can keep the amount of carbon in carbonic chain of molecules produced. Thus it is important that the catalyst used to present certain selectivity for de-oxygenation, HDOX, adding hydrogen energy to final product. This can be achieved with the use of catalytic with metal sites and high pressure of hydrogen gas.

Using only the thermal effect in the quality of the product becomes very limited, with low conversions and high production of coke. When selecting the catalyst that if you want to use if you need to look for the desired product. To produce diesel and heavy hydrocarbons, the size of the carbon chains of organic acids must be maintained, that the unsaturation should be saturated and the material should promote deoxygenation, what is achieved with metallic and neutral site. To produce gasoline and light hydrocarbons, carbon chains of oil must be fragmented, such a process is achieved with acid catalysts, promoting the fragmentation of chains, even though these have not unsaturation, where the sites also promote the deoxygenation.

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