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Robin, T, Jones, JM orcid.org/0000-0001-8687-9869 and Ross, AB (2017) Catalytic hydrothermal processing of lipids using metal doped zeolites. Biomass and Bioenergy, 98. pp. 26-36. ISSN 0961-9534

https://doi.org/10.1016/j.biombioe.2017.01.012

Catalytic hydrothermal processing of lipids using metal doped zeolites

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Keywords: hydrothermal processing, catalysis, HZSM-5, lipids, fatty acids

Abstract

A range of vegetable oils with different lipid compositions have been processed under hydrothermal conditions in the presence of transition metal doped zeolites (containing molybdenum, chromium, cobalt and iron). The lipids processed include sunflower, soybean, jatropha, palm and linseed oils over a temperature and pressure range of 250 to 350 °C and 12-17 MPa respectively. The products have been analyzed using a combination of GC-MS, FAME analysis, size exclusion chromatography (SEC), and simulated distillation (using thermogravimetric analysis TGA). Hydrothermal processing of lipids results in the hydrolysis of the triglycerides at low temperatures. Lipids high in polyunsaturated fatty acids such as linoleic and linolenic acid promote cross linking and cyclization reactions resulting in "heavier molecular weight" wax-like material. Saturated fatty acids such as palmitic and stearic acids are more stable. Some of the catalysts, such as un-doped zeolite (HZSM-5) and molybdenum doped zeolite (MoZSM-5) favor the formation of alkenes and aromatic compounds in the kerosene and gasoline boiling point range.

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1. Introduction

Oleaginous biomass such as microalgae are receiving increased attention as a feedstock to replace fossil fuels and may offer several advantages over conventional biomass. These include faster growth rates, lower land requirements and higher lipid contents than terrestrial oil seed crops [1]. There are numerous ways of converting microalgae into liquid transport fuels such as lipid extraction to produce biodiesel, hydrogenation of the lipids to produce 'green diesel' or direct liquefaction followed by subsequent upgrading. The latter includes an emerging technology called hydrothermal liquefaction (HTL) which involves conversion of wet whole biomass in hot compressed water and results in the production of a synthetic crude oil. A higher yield of bio-crude is produced compared to that from lipid extraction. This technology is also ideally suited to the processing of high moisture content biomass such as microalgae [2,3].

Hydrothermal liquefaction relies on the changing properties of water when heated to elevated temperature and pressure. For example, the dielectric constant of water decreases from 78 F/m at room temperature to 14 F/m at 350 °C resulting in an increase in the solubility of non-polar molecules in water [4]. The main challenges associated with hydrothermal liquefaction of microalgae include the reduction of nitrogen content in the bio-crude and reducing the molecular weight of the bio-crude oils. Understanding the degradation routes of the different biochemical components and subsequent reaction chemistry under hydrothermal processing conditions is therefore crucial in tackling these challenges. Biller et al. [2] indicated that the lipid fraction from the microalgae had the highest impact on the formation of the bio-crude oil. Understanding the degradation of lipids under hydrothermal conditions therefore provides insight into the liquefaction behavior of high lipid containing biomass such as microalgae.

A number of workers have investigated the hydrothermal degradation of lipids alone [5–7]. Hydrothermal treatment of triglycerides from soybean, linseed and coconut oils result in the formation of free fatty acids at temperatures of 260–280 °C, with 97 % of triglycerides becoming hydrolyzed below 300 °C in a batch reactor [5] with slightly higher temperatures being required in a continuous reactor [6]. The deoxygenation of model compounds in hot compressed water (300 °C, 25 MPa for 30 minutes) has shown that saturated carboxylic acids such as stearic acid are stable in subcritical water in the absence of a catalyst [8]. Several studies have investigated the hydrothermal deoxygenation of a mixture of sunflower oil and soybean stalk in a mass ratio (dry basis) of 4.4:1 [9–11]. The maximal hydrocarbon mass fraction of the resulting oil was 50.4 % at 400°C [10]. More recently, the behavior of lipids was studied in the presence of proteins and carbohydrates in order to have a better understanding of the hydrothermal degradation of microalgae [12,13].

The presence of catalysts are necessary to upgrade vegetable oils and fatty acids into hydrocarbons. Various catalysts have been investigated in different types of reactors (batch and continuous) to upgrade different fatty acids and vegetable oils such as carbon based catalysts [14,15], Nickel supported catalysts ($NiZrO_2$) [16] and noble metal based catalysts supported on carbon (Pd/C and Pt/C) [7,17]. However, acidic catalysts such as zeolites have been shown to be more suitable for producing lighter fractions from lipids. ZSM-5 is used widely in the petrochemical industry because of its acidity and shape selective nature due to its micro and mesoporous structure. ZSM-5 also possesses a high concentration of Lewis acid and Brønsted acid sites. HZSM-5 enhances the hydrothermal catalytic cracking of palmitic acid at 400 °C resulting in the production of a large range of hydrocarbons [18]. In a more recent study, HZSM-5 with a low Si/Al ratio of 23 was more selective for producing BTX aromatics (benzene, toluene and xylene) from palmitic acid at 400 °C compared to higher Si/Al ratio.

Higher conversion was achieved with the same catalyst compared to other acidic zeolites (HBeta and HY) [19].

The addition of transition metals to ZSM-5 by either ion exchange or impregnation has been investigated in a recent study by Robin et al. [20]. Metal doped ZSM-5 catalysts were more stable when prepared by ion-exchanged compared to impregnation. MoZSM-5 favored the deoxygenation of microalgae bio-crude and the formation of aromatic compounds from sunflower oil. From the foregoing discussion, the study of metal doped catalysts, including HZSM-5, MoZSM-5, FeZSM-5, CoZSM-5 and CrZSM-5 were carried out in more detail and the results compared to the previous study towards their activity and selectivity towards processing of lipids in subcritical water. Different vegetable oils containing a range of saturated, monounsaturated and polyunsaturated fatty acids were investigated. The influence of catalyst addition on the production of alkenes and aromatics is investigated. Product composition is compared with and without catalyst at a range of reaction temperatures for sunflower, linseed, soybean, jatropha and palm oil and model mixtures of polyunsaturated fatty acids (oleic, linoleic and linolenic acids) to assess the influence of saturation on reaction pathways. Finally, a mechanism for the hydrothermal processing of lipids is proposed and its implications for strain selection during hydrothermal liquefaction of microalgae.

2. Materials and Methods

2.1 Materials

Sunflower, soybean and palm oils are refined oils of food grade obtained from a local supermarket. Linseed oil was obtained from a local art supplier. Jatropha oil was unrefined. Oleic acid was purchased from alpha Aesar, linoleic and linolenic acids from Sigma Aldrich. Since the origin, processing and the chain of custody of the vegetable oils is unknown, it is

impossible to guarantee that the work can be repeated, we believe that the behaviour of the substrates used is representative of the relative behaviour between the oils, but the results may differ when other sources of these materials are used.

2.2 Analysis of raw vegetable oils

FAME analysis was performed to quantify the fatty acid composition of the raw vegetable oils and was performed as follows: 0.2 g of oil was mixed with 3 cm^3 of methanol and one drop of sulfuric acid (96 %) and heated to 60 °C for one hour. Once cooled, 2 cm^3 of water and 2 cm^3 of pentane was added to the solution and mixed. The pentane phase was separated and placed in a pre-weighed vessel and the pentane solvent was allowed to evaporate. The FAME (Fatty acid methyl ester) was dissolved in dichloromethane and analyzed by GC-MS (Agilent 5975B inert GC-MSD). The GC-MS was calibrated using FAME standards obtained from Sigma Aldrich. Separation of the products was achieved using an RTx 1701 60 m capillary column, 0.25 id, 0.25 µm film thickness using the following temperature program: 40 °C, hold time two minutes, ramped to 280 °C at 60 K min^{-1}, hold time ten minutes. The column head pressure was 308 kPa at 40 °C. FAME content is expressed in $g.kg^{-1}$ of oil. The compounds are identified using a combination of retention data and use of a NIST05a library database.

2.3 Catalyst preparation

The zeolite was purchased as NH_4-ZSM5 from Alfa Aesar. HZSM-5 was obtained by calcination of NH_4-ZSM-5 for three hours at 550 °C under a constant flow of air (50 cm^3/min). The Si/Al ratio was 27. The metal-exchanged catalysts were prepared by the method described by Long et al. [21]. Briefly, 20 g of NH_4-ZSM-5 was mixed with a 0.05 M solution of metal salts ($Fe(NO_3)_3$, $Co(acac)_2$, $Mo_7O_{24}(NH_4)_6$ and $Cr_2(CH_3CO_2)$) under constant stirring for 24

hours. The solid was washed and filtered under vacuum and subsequently dried at 110 °C. Finally, the doped zeolite was calcined at 550 °C for five hours. The chemical composition of the metal-exchanged zeolite was analyzed by ICP-OES (Induction coupled plasma-optical emission spectroscopy) following acid digestion in hydrofluoric acid (HF) and was determined to contain the following metal loadings with a statistical error of 2.0 %: FeZSM-5 0.34 %, CoZSM-5 0.21 %, MoZSM-5 0.14 % CrZSM-5 0.03 %. The characterisation of the catalysts and their hydrothermal stability is described elsewhere and are shown to be stable under hydrothermal conditions [20].

2.4 Hydrothermal processing

The hydrothermal processing of the vegetable oils was performed in an unstirred batch reactor (75 cm^3, Parr, USA). 0.5 g of catalyst, 3 g of vegetable oil (sunflower, soybean, linseed, jatropha and palm oils) and 27 cm^3 of deionized water was added to the reactor which was subsequently pressurized with 0.2 MPa nitrogen. The ratio of catalyst used and reaction time are consistent with conditions previously used to investigate the catalytic hydrothermal liquefaction of microalgae with alumina supported catalysts [22]. The reactor was heated to different temperatures (250, 300, and 350 °C) with a heating rate of approximately 9 $K.min^{-1}$. The reactor was held at the final temperature for one hour. Experiments were carried out in duplicate and the reproducibility in the mass balance of products is found to have a statistical error of 3%.

2.5 Sample workup and analysis

After cooling, the pressure was measured and the gas was released. The mass yield of the gaseous phase was measured according to Biller et al. [2] and is included in the supporting information. Once the reactor is opened, the content was poured into a beaker and the reactor

was successively rinsed with 50 cm^3 of deionized water and 50 cm^3 of dichloromethane (DCM). The two phases were each filtered to remove the catalyst and subsequently combined in a separating funnel and allowed to separate. The organic phase (DCM) was separated and filtered further and allowed to evaporate at room temperature to obtain the mass yield of bio-crude oil. The mass yield of the aqueous yield was measured by subtraction of the yield of the gaseous phase and the bio-crude and is included in the supporting information.

Following evaporation, a fraction of the bio-crude oil was re-dissolved in DCM using a 10 % concentration and analyzed by GC-MS using the same instrument and method with a split ratio of 1:10 described in section 2.2. A further sample of the bio-crude oil was converted to FAME

The boiling range of the bio-crude was estimated using thermogravimetric analysis (TGA) using a TA instrument (Q5000IR). A fraction of the bio-crude (10 mg) was heated from 40 to 900 °C at a heating rate of 10 K min^{-1} under nitrogen (50 $cm^3.min^{-1}$). The boiling curve was divided into 5 distinct boiling fractions; (i) the gasoline-like fraction (< 170 °C), (ii) the kerosene-like fraction (170 to 250 °C), (iii) the diesel-like fraction (250-350 °C), (iv) the vacuum diesel-like fraction (350-400 °C) and (v) residue (> 400 °C).

Size exclusion chromatography (SEC) of the bio-crude was performed using a Perkin Elmer series 200 HPLC (high pressure liquid chromatography) instrument as described elsewhere [20]. The SEC fractions were divided into 4 bands, “heavy molecular weight” materials (> 1000 g-mol^{-1}), the range corresponding to oligomers (1000-600 g-mol^{-1}), the range corresponding to the fatty acids (600-200 g-mol^{-1}) and the range corresponding to low molecular weight compounds (< 200 g-mol^{-1}).

3. Results

3.1 Chemical composition of the raw vegetable oils

The analysis of the crude vegetable oils is listed in **Table 1** and indicates that linseed, sunflower and soybean oils contain mainly polyunsaturated fatty acids (linolenic and linoleic acids) with a total fraction of 67.7, 44.9 and 50.1 % respectively. Jatropha oil contains a higher fraction of monounsaturated fatty acids with approximately 39.0 % of oleic acid. Palm oil, on the other hand, contains mainly saturated fatty acids with 48.0 % of palmitic and stearic acids. The average repeatability or statistical error was approximately 7.5 %. The theoretical molecular weight of the vegetable oils (**Table 1**) is calculated using **equation 1.**

$$\text{Average } Mw_{\text{vegetal oil}} = \left(3 * \left(\frac{\sum f_i}{\sum \frac{f_i}{MW_i}}\right) + 38.04\right) * x_{TAG} + \left(\left(\frac{\sum f_i}{\sum \frac{f_i}{MW_i}}\right) * y_{FFA}\right) \quad \textbf{Equation 1}$$

Where $Mw_{\text{vegetable oil}}$ is the theoretical molecular weight of the vegetable oils (g-mol^{-1}), f_i is the normalized composition of fatty acids, MW_i is the molecular weight of fatty acids, 38.0 g-mol^{-1} is the molecular weight of glycerol, x_{TAG} is the mass fraction in a specific size range and y_{FFA} is the % size range of the free fatty acid.

The molecular weight ranges measured by size exclusion chromatography (SEC) indicates that soybean, linseed and sunflower oils typically contain less than 90 % mass fraction of triglycerides, a small fraction of free fatty acids (2.0 %) and a small amounts of lower molecular weight material less than 200 g-mol^{-1} (possibly glycerol). For palm oil, the triglyceride content is 82.4 % with 4.2 % free fatty acids. Jatropha oil contains 73.1 % triglycerides and 11.6 % of free fatty acids. Palm and jatropha oils also contain approximately 9.0 % of material between 1000 and 600 g-mol^{-1} which is possibly diglycerides. Titration of

the raw oils give a similar value for the free fatty acid content with 10.2, 3.0 and 0.8 % for jatropha, palm and linseed oils respectively. The composition of the model mixtures are listed in **Table 1** and are prepared to simulate the composition of linseed, sunflower and jatropha oils. The theoretical molecular weight of the free fatty acids range between 256.4to 284.5 g-mol^{-1}, monoglycerides would be expected to have a molecular weight ranging between 294.4 and 322.5 and diglycerides would be expected to have a molecular weight ranging between 550.4 and 607.0.

Table 1: Chemical composition of the raw vegetable oils and mixtures

	% Mass fractions of fatty acid in oils [1]					% Mass fractions of PUFA, FFA and TAG[2]			Av. Mol. w (g/mol
	C16:0	C18:0	C18:1	C18:2	C18:3	PUFA	TAG	FFA	
Sunflower oil	14.6	13.8	27.3	43.7	0	43.7	93.8	2.0	822.7
Soybean oil	11.0	5.3	32.7	45.5	5.4	50.9	90.5	2.5	797.1
Linseed oil	6.9	8.2	16.7	11.7	56.0	67.7	96.0	1.5	841.8
Jatropha oil	12.3	15.8	39.5	32.4	0	32.4	73.1	11.6	671.2
Palm oil	39.3	9.6	39.9	11.3	0	11.3	82.4	5.3	717.1
Synthetic linseed	0	4.0	12.5	8.3	75.0	83.3			279.4
Synthetic sunflower	0	6.0	26.7	67.0	0	67.0			281.2
Synthetic jatropha	0	33.3	33.3	33.3	0	33.3			282.5

3.2 Effect of HTL temperature on oil composition

The SEC analysis of the bio-crudes produced from sunflower oil, linseed oil and palm oil at different reaction temperatures is shown in **Figure 1.** The results represent the mass fractions of the biocrude in each of four molecular weight fraction ranges and has an average statistical error of 5.0 %. The results from soybean and jatropha oils were not shown here as they are similar to the profile of sunflower and palm oils respectively. The data lists the normalized molecular weight range corresponding to the triglycerides or "heavy molecular weight" materials (> 1000 g-mol-1), the range corresponding to the oligomers (1000-600 g-mol-1), the range corresponding to the fatty acids (600-200 g-mol-1) and the range corresponding to low molecular weight compounds (lower 200 g-mol-1). The theoretical molecular weights of the lipids range from 670-820 $g\text{-}mol^{-1}$. The SEC analysis therefore slightly over estimates the molecular weight of the oils, possibly due to steric hindrance however the comparative analysis between the different conditions provides insight to the extent of decomposition.

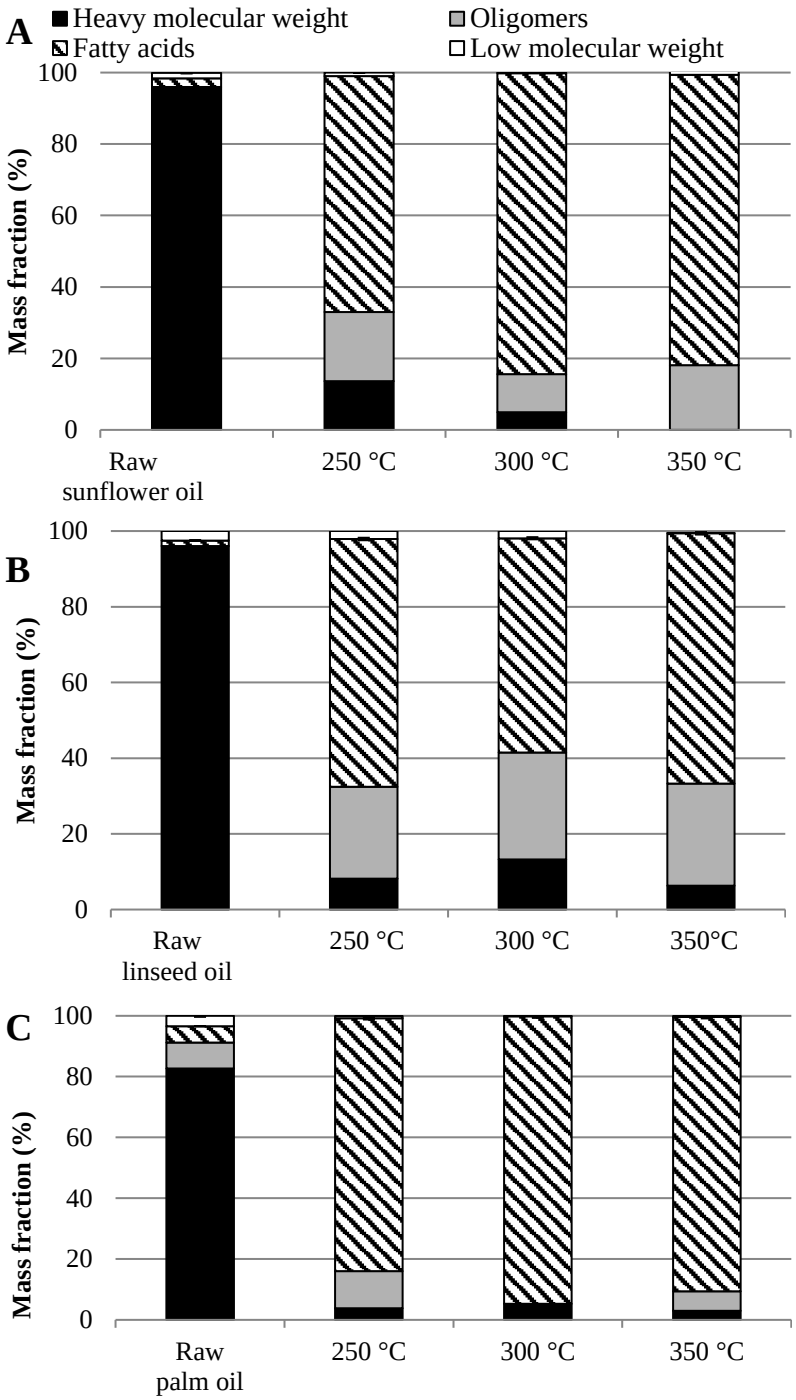

Figure 1: Different molecular weight fractions for **(A)** sunflower, **(B)** linseed, **(C)** palm oils at different temperatures without catalyst for one hour. Heavy molecular weight (> 1000 g/mol), Oligomers (1000-600 g/mol), Fatty acids (600-200 g/mol), lower molecular weight (200 g/mol).

The SEC analysis indicates a reduction in molecular weight following hydrothermal treatment for each of the vegetable oils (sunflower, soybean, jatropha and palm oils). The majority of the triglycerides are converted to lower molecular weight material at temperatures

above 250 °C to form products such as diglycerides and wax-like oligomers (molecular weight between 1000 to 600 g-mol^{-1}), fatty acids or long chain aliphatic compounds (molecular weight between 600-200 g-mol^{-1}), with the exception of linseed oil which still contains "heavy molecular weight" material even at 350 °C. This is proposed to be due to cross linking reactions and is associated with the reaction of polyunsaturated fatty acids [23]. The levels of free fatty acids increase as the temperature increases, although there is still evidence for triglycerides at 250 °C. Previous studies have shown hydrolysis of triglycerides occurs in a similar temperature range and that the rate of hydrolysis increases with reaction temperature [24-25].

Figure 1C shows the results for palm oil and indicate the main size fraction remaining after 250 °C corresponds to free fatty acids with 83.2 % and 85.9 %, respectively. The other fractions are attributed to diglycerides or wax-like oligomers (around 10 %). At 300 °C, the main size fraction remaining is predominantly free fatty acids (approximately 95 %) with lower amount of oligomer materials. The levels of free fatty acids for the linseed, soybean and sunflower oils at 250 °C are lower. This suggests that palm and jatropha oils are hydrolyzed at a lower temperature than linseed, soybean and sunflower oils. As the temperature increases to 300 °C, the fraction with a molecular weight between 600 to 1000 g-mol^{-1} reduces considerably. At higher temperatures approaching 350 °C, the fraction of higher molecular weight material begins to increase indicating possible cross linking reactions producing wax-like oligomers.

The SEC analysis after hydrothermal treatment provides relative values for the change in molecular weight. The molecular weight of the products are expected to be slightly over estimated in a similar manner to the starting oils shown in **Table 1**. Despite this, the data is still useful and shows that following hydrothermal treatment, the molecular weight range is

reduced. This can be used, together with boiling point data provided by TGA in **Table 2** to show the decomposition of lipids to diglycerides, monoglycerides and free fatty acids.

The propensity for cross linking was investigated further using model mixtures of free fatty acids containing different levels of polyunsaturated fatty acids. **Figure 2** shows the molecular weight breakdown of the HTL products from the individual free fatty acids (oleic, linoleic and linolenic acids) and the synthetic lipid mixture at 350 °C. The results indicate that the levels of oligomers formed increase as the levels of unsaturated fatty acids increase. This is observed for both the free fatty acids processed alone and the model lipid mixture. Increased levels of oligomers are obtained for the linoleic (28.8 %), and linolenic acid (32.0 %) compared to the oleic acids (2.8 %). The results observed from the synthetic mixture of linseed oil show a similar profile to that of linseed oil. The "heavy molecular weight" material is proposed to be due to polymerization of fatty acids, whereas oligomers are the results of intra-cyclization reactions. The results suggest there is a link between the levels of saturation of the fatty acids and the presence of "heavy molecular weight" materials in the bio-crude. Teri et al. [12] observed that the formation of "heavy bio-crude" was more significant processing castor oil compared to sunflower oil at 350 °C and proposed that this was due to castor oil containing more polyunsaturated fatty acids.

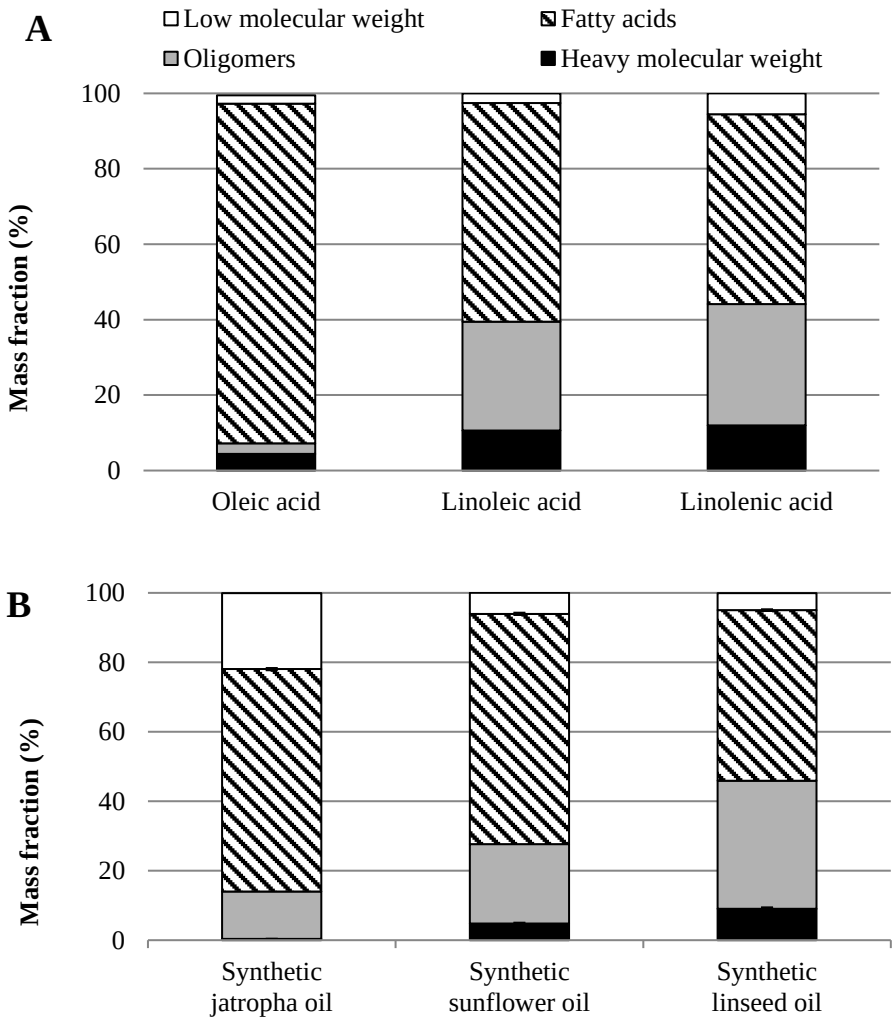

Figure 2: Molecular weight distribution of oils analysed by size exclusion chromatography (composition calibrated by polystyrene in solvent THF) where **(A)** the fatty acid mixtures alone processed at 350 °C and **(B)** the synthetic mixtures with different fatty acid content

Transesterification of the fatty acids to FAME is performed for each of the bio-crudes generated to enable analysis of the fatty acid profiles. The overall profile of the fatty acids is significantly affected by the increase in temperature from 250 to 350 °C. **Figure 3** shows the fatty acid content of the oils before and after hydrothermal treatment for sunflower oil, linseed oil, and palm oil. As previously, the figure of soybean and jatropha oils are not shown as they are relatively similar to sunflower oil and palm oil respectively.

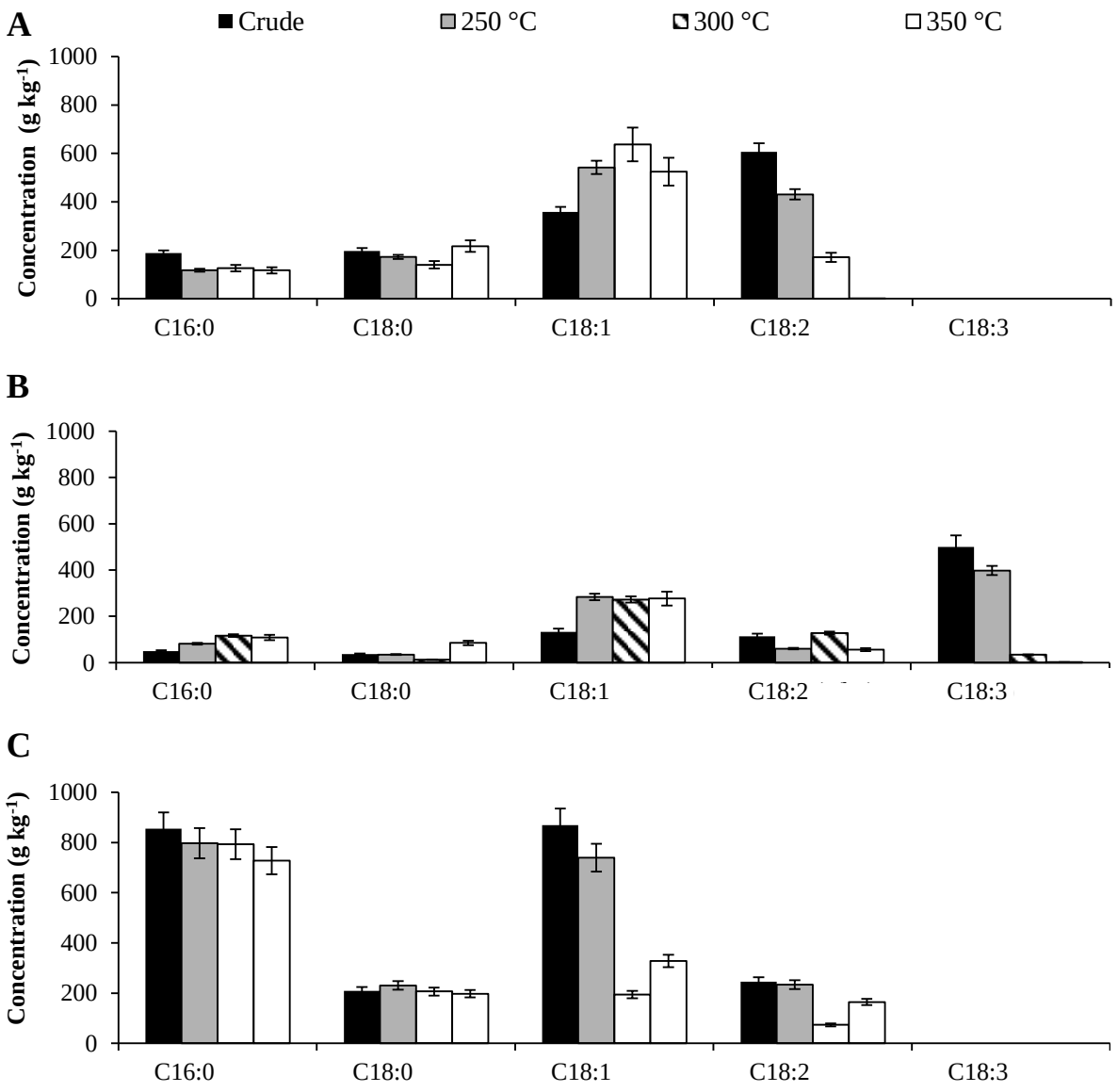

Figure 3: Normalised fatty acid distribution of oils following hydrothermal liquefaction at different temperatures without catalyst for one hour for **(A)** sunflower oil, **(B)** linseed oil, **(C)** palm oil.

The levels of polyunsaturated linolenic and linoleic acids, for example in linseed oil (Figure **3B**), decrease as the temperatures increases, although this becomes more significant at temperatures above 300 °C. At 350 °C, most of the linolenic and linoleic acids are absent. A similar trend is observed with sunflower and soybean oils (Figure **3A**), where the levels of

linoleic acid decrease as the temperature increases beyond 250 °C. These results are more similar to previous studies [8, 26]. The FAME analysis of the processed linolenic acid (not shown in the diagram) indicates that none of the original fatty acids have been recovered at 350 °C. The reactivity of this fatty acid can be explained by its cross linking. Linolenic acid can also decompose into 9-(o-propylphenyl)-nonanoic and methyl-2-octylcyclopropene-1-heptanoate. Only 11 % of linoleic acid can be recovered after processing at 350 °C. Linoleic acid mainly decomposes by delocalization of the double bonds into 8,11-octadecadienoic, 11,14-octadecadienoic acids. Other products formed by the decomposition of the oils high in linoleic acid include aldehydes such as hexadecadienal, alcohols such as octadecadienol and alkenes such as 8-heptadecene.

The oleic acid is relatively stable as demonstrated by Shin et al. [29] and only begins to decrease as the temperature reaches 350 °C. For sunflower oil, there is a corresponding increase in the levels of oleic acid as the temperature increases. For the jatropha and palm oils, the levels of oleic acid decreases, probably caused by the cross linking with linoleic acid. High amounts of oleic acid can be recovered after the processing at 350 °C (66 %).

Saturated fatty acids (palmitic and stearic acids) are stable under subcritical water, as shown in previous studies [19,26]. Fujii et al. [27] demonstrated that fatty acids commonly only start to degrade above 300 °C. For palm and jatropha oils, which contain largely saturated fatty acids, the levels of palmitic and stearic acids are relatively stable even up to 350 ^{o}C however the polyunsaturated content reduces as the temperature increases

Previous studies suggested that this reduction in polyunsaturated fatty acids was due to hydrogenation of the unsaturated fatty acids to more saturated analogues [2]. However, the results from this study suggest there are additional reactions occurring responsible for their

apparent reduction resulting in “heavy molecular weight” material. The higher levels of saturated hydrocarbons and the proposed formation of wax-like oligomers explain why the oils obtained are viscous and appear as ‘wax-like’ solids at room temperature.

In summary, the temperature has an effect on the profile of fatty acids after hydrothermal processing, especially for vegetable oils containing polyunsaturated fatty acids (sunflower, soybean and linseed oils). The hydrolysis of the lipids into fatty acids begins at temperatures above 250 °C. At higher temperatures, the lipids containing higher levels of unsaturation result in an increase in “heavy molecular weight” materials via the cross linking of the polyunsaturated fatty acids. The justification for this work is to develop an understanding of the degradation routes of lipids and its implications for the hydrothermal liquefaction of microalgae. The biochemical composition of different microalgae vary widely and are significantly affected by the cultivation conditions. The composition of the lipid fractions also varies and it is not uncommon for microalgae to contain large amounts of polyunsaturated fatty acids [28]. Microalgae also contain significant levels of glycolipids, phospholipids and pigments which will complicate reaction pathways. Despite this the results provide insight into ways for tackling one of the challenges of HTL by reducing the molecular weight of the bio-crude. [12].

3.3 Influence of metal doped zeolite catalysts on oil composition

3.3.1 Mass yield and elemental analysis

The mass yield of bio-crude oil and the ultimate analysis and CV of the biocrudes produced with and without catalysts are listed in **Table 2**. The Heating value of the bio-crudes were determined using the Dulong formula [31]. The analysis was performed in duplicate and

have an average statistical error of 2.5 %. For the yields of products, the statistical error was 3.0 %.

Table 2: Elemental mass fraction of oils, HHV (MJ kg^{-1}) and mass yield of biocrude.

	C (%)	H (%)	O (%)1	Oil HHV ($MJ.kg^{-1}$)	Mass yield
raw sunflower oil	**72.9**	**11.1**	**16.0**	**37.6**	**-**
250 °C	**77.1**	**12.0**	**10.9**	**41.3**	**74**
300 °C	**78.0**	**11.43**	**10.6**	**40.8**	**87**
350 °C	**76.8**	**11.49**	**11.7**	**40.3**	**86**
HZSM-5	**80.4**	**11.9**	**7.7**	**42.8**	**68**
MoZSM-5	**80.0**	**11.6**	**8.4**	**42.1**	**60**
FeZSM-5	**75.5**	**11.4**	**13.1**	**39.5**	**58**
CrZSM-5	**77.0**	**11.7**	**11.3**	**40.7**	**70**
CoZSM-5	**78.5**	**11.9**	**9.6**	**41.8**	**63**
Raw linseed oil	**72.8**	**11.3**	**16.0**	**37.9**	**-**
250 °C	**77.8**	**10.7**	**11.5**	**39.5**	**91**
300 °C	**74.7**	**10.4**	**14.9**	**37.5**	**99**
350 °C	**75.2**	**10.3**	**14.5**	**37.5**	**93**
HZSM-5	**79.3**	**13.5**	**10.0**	**44.3**	**81**
Raw soybean oil	**75.5**	**12.6**	**11.9**	**41.4**	**-**
250 °C	**79.8**	**11.6**	**8.5**	**42.1**	**90**
300 °C	**79.9**	**11.4**	**8.7**	**41.8**	**95**
350 °C	**79.0**	**11.2**	**9.7**	**41.0**	**91**
HZSM-5	**80.7**	**11.3**	**8.0**	**42.0**	**79**
Raw jatropha oil	**76.5**	**12.4**	**11.1**	**41.5**	**-**
250 °C	**78.3**	**11.4**	**10.3**	**40.9**	**89**
300 °C	**69.2**	**11.1**	**19.7**	**35.7**	**89**
350 °C	**68.3**	**12.6**	**21.7**	**37.2**	**93**
HZSM-5	**66.5**	**12.1**	**23.9**	**35.5**	**77**
Raw Palm oil	**77.4**	**12.2**	**10.3**	**41.8**	**-**
250 °C	**73.1**	**11.9**	**14.9**	**39.1**	**89**
300 °C	**73.2**	**11.0**	**15.9**	**37.6**	**88**
350 °C	**72.0**	**11.6**	**16.4**	**38.0**	**90**
HZSM-5	**76.3**	**12.3**	**11.4**	**41.4**	**79**
HTL oleic acid	**77.9**	**12.5**	**9.6**	**42.5**	**97**
HTL linoleic acid	**77.1**	**8.3**	**14.6**	**35.3**	**92**
HTL linolenic acid	**71.7**	**10.2**	**18.1**	**35.6**	**93**
Mixture sunflower	**80.0**	**10.0**	**10.0**	**39.5**	**86**
Mixture linseed	**75.4**	**11.1**	**13.5**	**38.9**	**86**
Mixture jatropha	**78.2**	**12.26**	**9.4**	**42.3**	**73**

1 Wt% oxygen was determined by the difference of the carbon and the hydrogen

The mass balance indicates that in the absence of a catalyst, the mass yields are typically 85 % of the input vegetable oil. The mass yields of bio-crude are consistently lower in the presence of a

catalyst with the exception of chromium. The yield from the HTL of sunflower oil for instance drop to as low as 58 % using a FeZSM-5 catalyst. The bio-crude yield using the catalyst support alone are higher for soybean, palm, jatropha and linseed oils compared with 68 % for sunflower oil. The processing of vegetable oils with ZSM-5 enhanced the formation of the gaseous and aqueous phases, these results are included in the **supporting information (Table 1)**.

A comparison of the composition of different vegetable oils and their resulting bio-crudes indicates that the carbon and hydrogen content in the bio-crude oil is increasing. The oxygen content is therefore reduced and the heating value is increased. The lowest oxygen content is obtained with the HZSM-5 support alone (7.7 %), and the MoZSM-5 (8.4 %). This reduction in oxygen content using HZSM-5 is observed for sunflower, soybean and linseed oil however for jatropha and palm oil, an increase in oxygen content is observed due to the reduction of the carbon content. Most of the heating values for resulting bio-crudes are above 40.0 MJ/kg, which is close to that of crude oil (4~2.2 MJ/kg).

For experiments without catalysts, the oxygen content of the resulting bio-crudes also increases between 250 to 350 °C, for example with soybean oil, the oxygen content is increased from 8.5 to 9.7 %. The possible explanation is the hydrolysis of triglyceride to free fatty acids and the removal of glycerol in the process water. The oxygen content of the bio-crude from linoleic and linolenic acids are higher at14.6 and 18.1 % respectively than the raw unsaturated fatty acids (approximately 11.4 %), there is also evidence for the formation of heavy molecular weight" material produced due to cross linking.

3.3.2 Chemical analysis

In the absence of any catalyst, there is very little cracking to lower molecular weight material such as aromatics, although alkanes and oxygenated compounds are present. Alkenes can be identified, but at low levels (approximately 5.0 %). This suggests that without the use of a catalyst, only a limited amount of decarboxylation of fatty acids is being promoted. The bio-crude oil largely contains free fatty acids and long chain hydrocarbons. This agrees with previous studies, for example the decomposition of palmitic acid at 370 °C produces less than 2.0 % pentadecane in the absence of a catalyst [7]. The results from this work support the claim that in the absence of a catalyst, the saturated fatty acids are relatively stable.

Analysis of the oils by GC-MS is shown in the **Supplementary Material (Figure 1)**. The products can be broadly divided into three main groups: aromatic and short chain alkanes compounds (octane to dodecane) (gasoline range) such as (1) o-xylene, (3) decene; (4) 1-ethyl-2-methyl-benzene; (13) 1-methyl-2-methylene-cyclohexane; (14) 1-methyl-3-hexyl-benzene; long chain alkenes (isomers of heptadecene) and long chain aldehydes including (16) tridecanol; (17) 3-heptadecene; (18) 8-heptadecene; (20) Z,Z-10,12-hexadecadienal; and heavier molecules attributed to fatty acids and esters (24) oleic acid; (26) Z,Z-9,12-octadecadienoic acid.

Figure 4 presents the percentage of each of these main groups based on normalized peak areas of compounds and allows a semi-quantitative comparison of the influence of the catalysts on the hydrothermal degradation of sunflower oil. It can be seen that the HZSM-5 and MoZSM-5 catalysts result in the highest activity for promoting the production of aromatic compounds and is in agreement with previous reports by Robin et al. [20]. The use of these catalysts also yield a greater fraction of C_8-C_{12} alkanes. The Brønsted acidic sites of the zeolites

are known to promote the production of more cracked products. MoZSM-5 appears to be more selective for aromatic and alkene compounds. Aromatic compounds are thought to be mainly produced via the Diels-Alder reactions or by radical pathways [23]. Toluene, xylene, propyl-benzene and 1,2,4-trimethyl-benzene were produced during the processing of fatty acids (palmitic, stearic acids) with HZSM-5 at 400 °C [19]. In the case of catalytic hydrothermal processing, analysis by GC-MS indicates that the majority of the hydrocarbons identified are alkenes, therefore, hydrogenation of the oils should be performed to obtain alkanes.

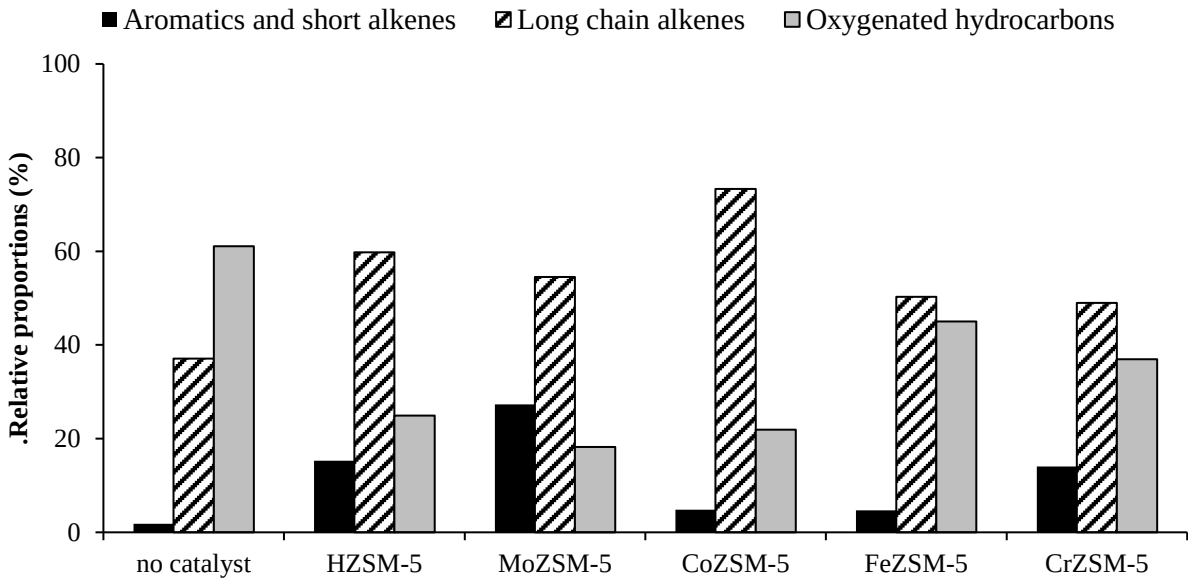

Figure 4: Breakdown of the oils following catalytic hydrothermal processing at 350 °C of sunflower oil for one hour into fractions of different chemical class.

FAME analysis of the sunflower oils treated with the different doped HZSM-5 is shown in **Figure 2A** contained in the **Supplementary materials** together with the processing of linseed, soybean, jatropha and palm oils with HZSM-5. The results indicate that all catalysts reduce the level of linolenic acid and that the HZSM-5 support alone and the CoZSM-5 reduces the levels of oleic acid. In addition to the effect on the free fatty acid composition, the levels of other compounds (non-FAME) are also increased with the formation of smaller cracking products as explained previously.

As the levels of oleic acid in the products decrease, the levels of heptadecene increase due to the decarboxylation of oleic acid. GC-MS and FAME analysis indicate a reduction of methyl oleate and the appearance of heptadecene. Similar behavior is observed for sunflower oil and HZSM-5 at the same temperature. The degradation of oleic acid to hydrocarbons has previously been observed under supercritical water (400 °C) with HZSM-5 although palmitic acid was found to be more selective towards the production of aromatic compounds [19]. Similar results in subcritical water (350-400 °C) were observed with a rapid conversion of oleic acid first to stearic acid and subsequently to heptadecane in the presence of activated carbon and formic acid as a supply of hydrogen [29]. The increase in saturation and decarboxylation influence the ability to subsequently upgrade the oil and influence the amount of hydrogen consumption required.

3.3.3 Boiling point analysis

The activity of the catalysts has also been assessed by measuring the boiling point distribution of the bio-crude oil generated at 350 °C using TGA. The boiling fractions of the oil can be determined from the boiling curve determined by TGA which shows the weight loss of oil vs temperature in a constant flow of nitrogen. It is expected that some coking will occur at higher temperatures however the technique provides a comparative assessment of the influence of the different catalystsThe results from the simulated distillation method are listed in **Table 3**.

Table 3: Normalised area fractions (%) measured by TGA and determined by weight loss of oils from the hydrothermal processing of sunflower oil and other vegetable oils in water at 350 °C with different catalyst

Vegetable oils: catalyst	Gasoline-like ≤ 170 °C	Kerosene-like 170-250 °C	Diesel-like 250-350 °C	Fuel oil-like 350-400 °C	Residue ≥ 400 °C
Raw sunflower oil	**0.0**	**2.9**	**37.7**	**14.2**	**45.2**
Raw soybean oil	**0.4**	**0.8**	**10.4**	**86.9**	**1.6**
Raw linseed oil	**0.4**	**1.1**	**8.0**	**90.1**	**0.5**
Raw jatropha oil	**0.0**	**2.4**	**9.2**	**9.5**	**78.1**
Raw palm oil	**2.3**	**3.4**	**18.2**	**75.6**	**0.5**
Sunflower oil: no catalyst	**1.9**	**62.8**	**26.8**	**1.6**	**6.9**
Sunflower: HZSM-5	**8.8**	**81.0**	**7.0**	**0.6**	**2.6**
sunflower: MoZSM-5	**16.1**	**71.1**	**9.0**	**0.6**	**3.2**
sunflower: CoZSM-5	**5.3**	**69.7**	**18.4**	**1.1**	**5.5**
sunflower: CrZSM-5	**3.9**	**73.3**	**17.2**	**0.9**	**4.8**
Sunflower: FeZSM-5	**3.6**	**23.9**	**61.5**	**3.6**	**7.3**
Soybean oil : HZSM-5	**5.5**	**78.3**	**7.9**	**1.0**	**7.3**
Linseed oil : HZSM-5	**2.9**	**55.0**	**15.0**	**2.8**	**24.4**
Jatropha oil : HZSM-5	**2.7**	**81.7**	**9.0**	**1.2**	**5.4**
Palm oil : HZSM-5	**3.2**	**88.7**	**3.5**	**1.1**	**3.1**

The raw sunflower oil has a higher boiling point range than the HTL products as expected. HTL in water alone produces an oil oil containing a large kerosene mass fraction (62 %). Nevertheless, when processed using catalysts, the level of the gasoline fraction increases. The highest yield of gasoline fraction is for the MoZSM-5 catalyst (16.1 %) although the HTL of sunflower oil with HZSM-5 (with no metal doping) produces the next highest gasoline fraction of (8.8%). For each of the catalysts, the main boiling fraction is still in the kerosene-like fraction. The metal doped catalysts also influence the diesel fraction. Typically, the presence of catalyst

reduces the diesel-like fraction (250-350 ^{o}C) with the exception of FeZSM-5. This catalyst is significantly different and promotes a significant increase in the diesel fraction (61.5%) with a resulting decrease in the kerosene-like fraction.

In order to determine the reactivity of HZSM-5 towards lipids with different levels of saturation, a series of experiments were performed for palm, jatropha, linseed and soybean oils at 350 °C. The boiling point fractions of the raw oils are listed in **Table 3** together with the results for processing at 350 ^{o}C with HZSM-5. The boiling point distributions of the raw oils show that the lipids are largely distributed in the 350-400 ^{o}C region. The boiling curves for the products following hydrothermal processing show that the largest fraction is still the kerosene-like fraction (170-250 ^{o}C) which is highest for Palm oil (88.7 %) and lowest for Linseed (55 %) suggesting that the level of saturation has a major influence on the boiling fraction of the products. Linseed oil also produces a significantly higher level of residual material (>400 ^{o}C). It is proposed that this is due to wax-like gums produced from the cross linking of the polyunsaturated fatty acids. The sunflower oil produces the highest levels of gasoline-like material (8.8%) followed by soybean (5.5 %), palm (3.2 %), linseed (2.9 %) and jatropha (2.7 %). .

4. Discussion

Chain cleavage can only occur inside the zeolite via β-scission of the fatty acids. Most of the reactions involved in subcritical water are ionic and are enhanced by the high acidity of HZSM-5 [30]. Inside the pore, carboxylic acids are hydrolyzed by Brønsted acid sites and the oxygen of the carbonyl is coordinated by the Lewis acid groups which, in this case are the aluminum or doped metal (cobalt or molybdenum). Cobalt is more selective towards decarboxylation because it can coordinate with the carbonyl groups (C=O) and can enhance

the rate of decarboxylation [31]. It can therefore be concluded that HZSM-5 and its metal doped derivatives can improve the decarboxylation or cracking of fatty acids. HZSM-5 can also be selective towards the production of propene from the deoxygenation of glycerol [32].

The SEC data demonstrates that the conversion to diglycerides or free fatty acids is complete in the absence of a catalyst. Following hydrolysis of the triglyceride, linoleic acid cis-9,12 can undergo a conjugation to cis-10,12. A cyclization of this molecule with an olefin can subsequently take place via the Diels-Alder reaction, even without a catalyst [33]. Scission of the alkyl groups branched to the benzene ring followed by reduction, results in the formation of trialkyl benzene. The orientation of the substituted alkyl groups is generally 1,2,3 and 1,4. The unconjugated form 10,12-octadecadienoic can also be reduced to form the aldehyde Z,Z-10,12-hexadecadienal [23]. The type of isomer present also effects the direction of the reaction, for instance the breakdown of the cis-form of oleic acid produces undecene and the trans-form produces heptanoic acid [26]. Mono substituted aromatic compounds are also formed by endo-cyclization and di-substituted aromatics can also be formed by exo-cyclization such as 1-ethyl-2-methyl-benzene which is formed by the cyclization of nonene [34,35]. One possible mechanism for the formation of aromatics is therefore the degradation of linoleic acid to smaller dienes followed by subsequent Diels-Alder reactions to form tri 1,2,3 substituted analogues or 1,3-di-substituted analogues such as 1,3-ethyl-dimethyl-benzene.

Furthermore, it is possible that the unsaturated fatty acids can undergo oxidization and polymerization forming long epoxy chains during storage. It is possible that the formation of wax-like material by cross linking is enhanced by the slow heating rates (9 °C/min) and the long cooling rates [36].

In hot compressed water below 280 °C, the isomerization of linolenic acid cis,cis,cis into trans,cis,cis is observed. Approximately 40-60 % of the original linolenic acid undergoes geometric isomerization [5]. The formation of inter-cyclization of unsaturated fatty acids such as linolenic acid can produce cyclopentan-octanal-2-octonyl and methyl-2-octylcyclopen-1-heptanal during the "frying process" [37]. The reaction involves a sigma-tropic rearrangement (1,5) between the carbon 3 and 6 of the chain forming a penta-cycle via a radical mechanism [37]. Under hydrothermal conditions, these compounds were also produced [23]. Three of the unsaturated fatty acids (oleic, linoleic and linolenic acids) can undergo inter-cyclization forming a C_5 or C_6 cycles. This process would reduce the number of double bonds and explain the apparent reduction in unsaturated fatty acids [23]. In this study, the aromatic compounds formed 9-(o-propylphenyl)-nonanoic and methyl-2-octylcyclopropene-1-heptanoate is identified from the degradation of linolenic acid from linseed oil. In the future, kinetic studies of different polyunsaturated fatty acids should be investigated to have a better comprehension of their degradation under hydrothermal water [38].

Thus, it is proposed in **Figure 5** that there are four main steps in the decomposition of lipids during hydrothermal liquefaction: the first step (reaction 1) involves the hydrolysis of triglyceride into fatty acids and glycerol, at a temperature below 250 °C this step proceeds without a catalyst. The second step (2) involves inter-cyclization reactions of unsaturated fatty acids to produce for example 9-(o-propylphenyl)-nonanoic acid. The third step (3) involves the formation of dimers with for example the intra-cyclization via Diels-Alder between linoleic and oleic acids. The fourth step (4) involves the decarboxylation of fatty acids into aldehydes and alkenes.

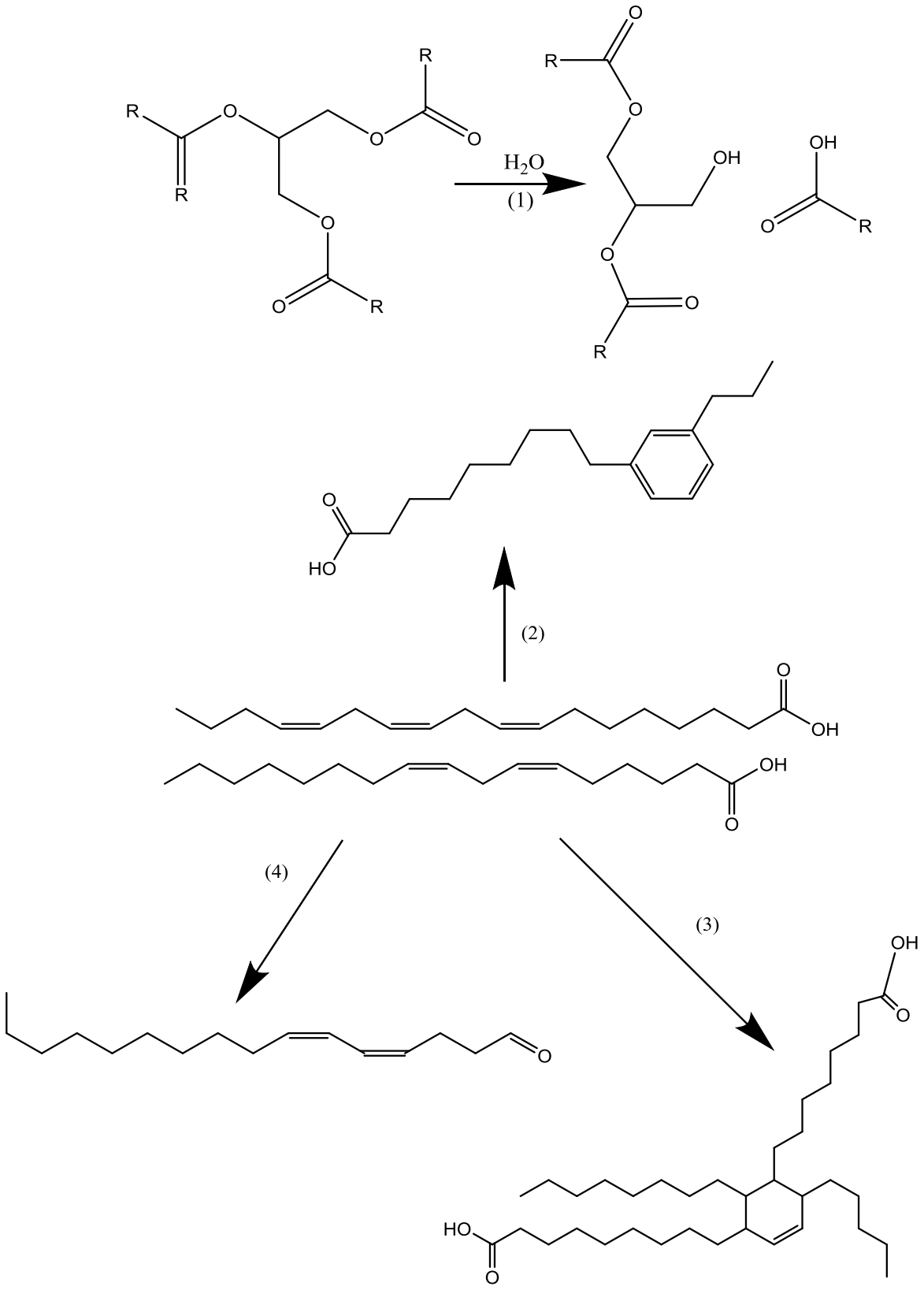

Figure 5: Proposed reaction pathways during the hydrothermal liquefaction of vegetable oils from 250 to 350 °C where (1) represents the first step of the hydrolysis of the triglycerides; (2). is the formation internal cycle, (3) is the production of oligomers from cross linking

(inter reaction between polyunsaturated fatty acids, (4) is the reduction of fatty acids into aldehyde

The challenge facing hydrothermal liquefaction is to be able to produce low molecular weight oil, which has suitably low oxygen, nitrogen and sulfur contents. The use of zeolites can crack the lipid fractions, and increase the gasoline fraction which ultimately improves the flow properties of the resulting oils. The bio-crude however still requires further upgrading and hydrogenation and isomerization must still be performed in a subsequent upgrading step. The higher fractions of unsaturated fatty acids and alkenes reduce stability. This may be compounded when processing the whole biomass, as the reactions will also involve fragments of proteins and carbohydrate degradation as well as glycolipids and phospholipids. Furthermore, when the lipid is associated with proteins, the formation of amides are favored [12]. In a similar manner to biodiesel production, microalgae with saturated or monounsaturated shorter chain fatty acids are favored as these reduce the potential for retrograde reactions. The use of zeolites will increase the aromatic content derived from the lipids and this will improve the quality of the bio-crude produced.

Metals doped zeolites exhibit activity towards cracking, despite their low metal loading [20]. Zeolites doped with Mo show particular promise for producing gasoline –range hydrocarbons. Methods of catalyst preparation may be improved resulting in enhance activity. The results from this study show that oil quality is enhanced using lipids high in monounsaturated fatty acids and suggests that significant improvement in oil quality can be gained by selecting microalgal strains with low levels of polyunsaturated fatty acids.

5. Conclusions

Triglycerides undergo hydrolysis into free fatty acids and glycerol under hydrothermal conditions below 250 °C. The levels of linoleic and linolenic acids in linseed, sunflower and

soybean oils are reduced as the temperature increases. High levels of unsaturated fatty acids promote the formation of higher molecular weight molecules. Zeolites promote cracking reactions to produce aromatic compounds and aliphatic hydrocarbons. The metal doped zeolites while containing low levels of metals have significantly different activity. The MoZSM-5 and HZSM-5 catalysts are more selective for producing lighter fractions in the gasoline range (aromatic and alkenes) whereas FeZSM-5 promotes the production of heavier material in the diesel range. Sunflower oil is more reactive compared to other vegetable oils with HZSM-5. The lower the level of polyunsaturated hydrocarbons, the lower the temperature required for hydrolysis.

6. Acknowledgements

The authors would also like to thank the Engineering and Physical Sciences Research Council (EPSRC) for supporting the PhD scholarship for Thomas Robin (EP/I014365/1). In addition the authors are grateful to Simon Lloyd, Dr Amanda Lea-Langton and Dr Adrian Cunliffe for technical support.

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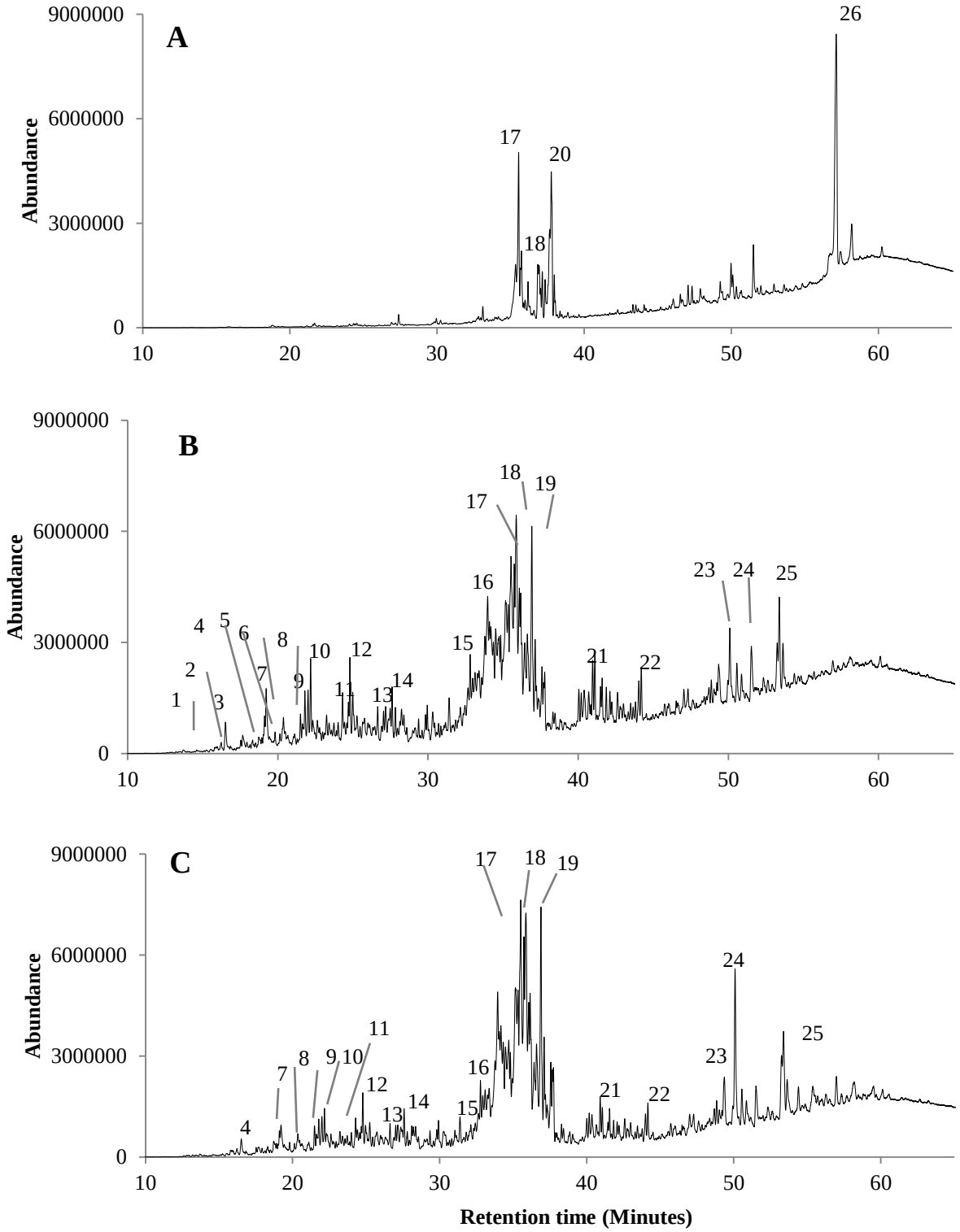
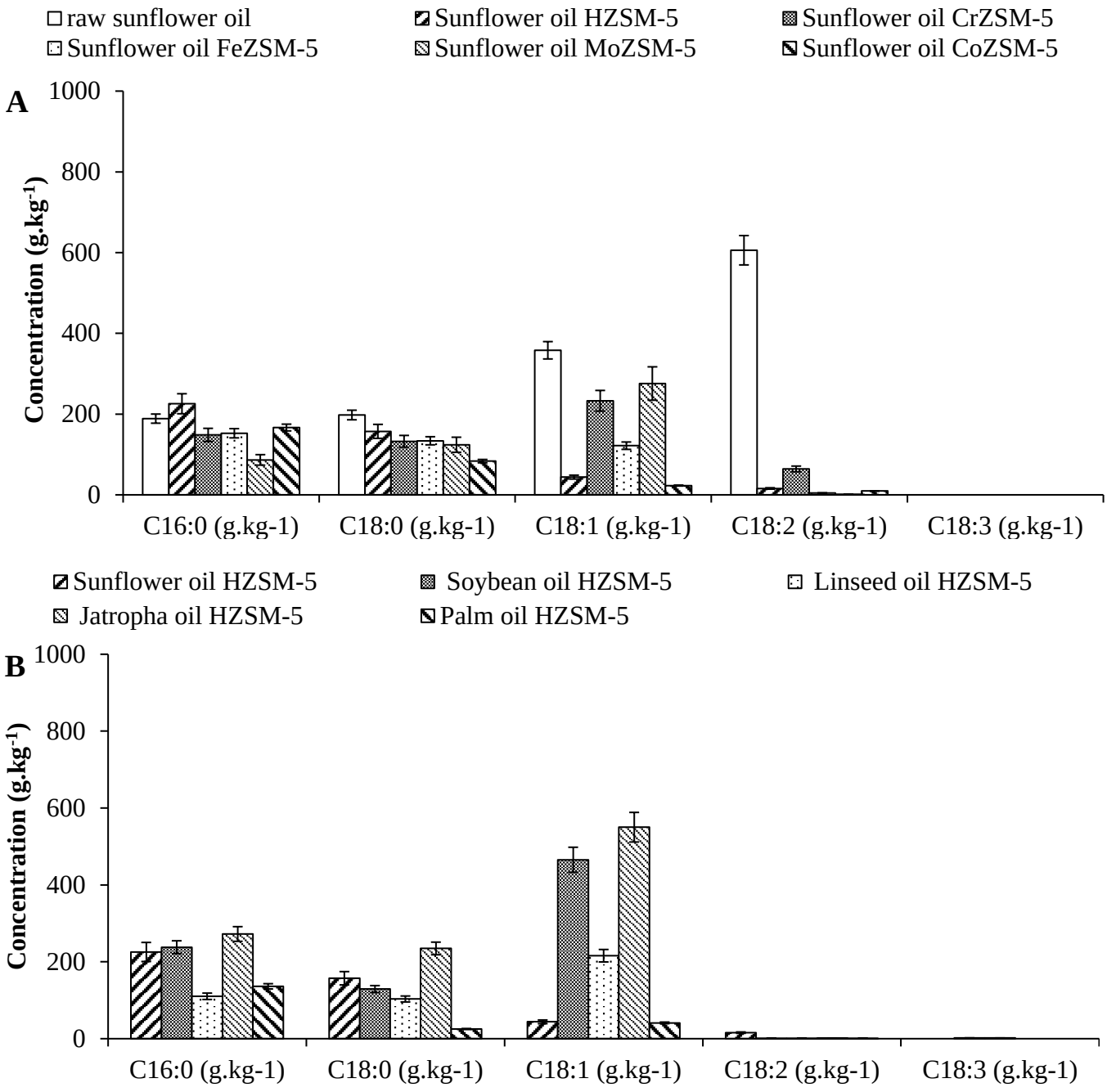
1. Supplementary Data

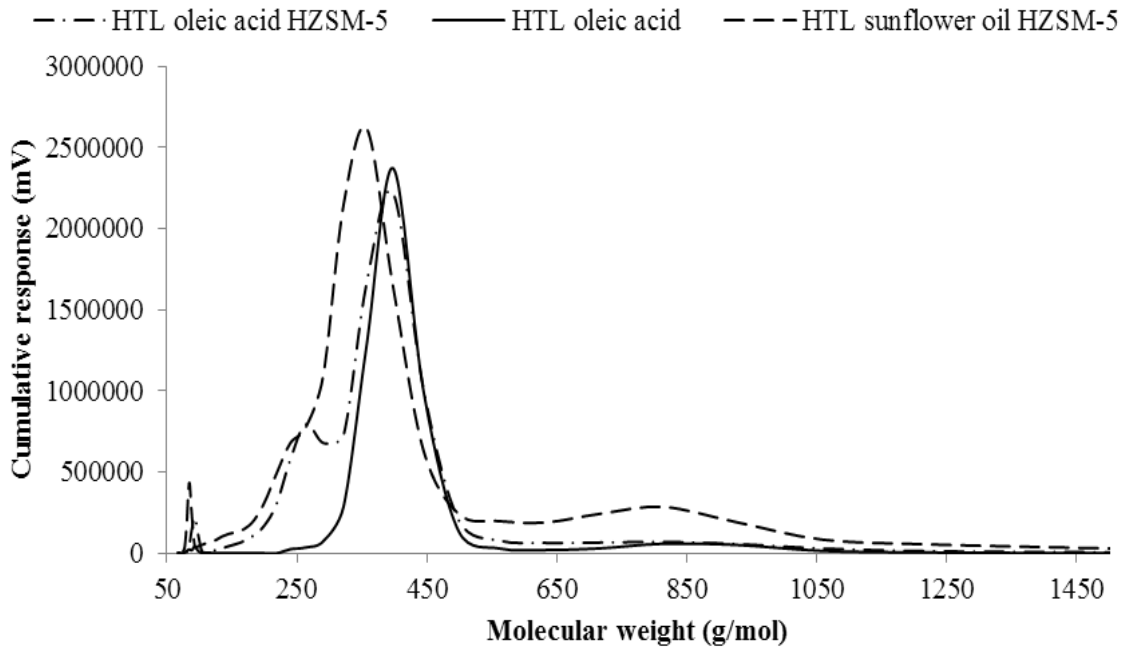


Supplementary Figure 1: GC-MS chromatograms of oil from hydrothermal processing of sunflower oil at 350ºC in **(A)** water alone without a catalyst, **(B)** in the presence of MoZSM5 catalyst and **(C)** in the presence of the HZSM5 support

(1) rt=12.8 min: o-xylene; (2) rt= 14.7 3-ethyl-2-pentene; (3) rt= 16.5 min Decene; (4):rt=17.4 min 1-ethyl-2-methyl benzene; (5): rt= 18.2 min 3-undecene (6): rt= 19 min 4-undecene; (7) rt= 19.2 min 1-methyl-3-propyl-benzene; (8) rt= 19.8 min Decalin, (9) rt = 21.8 min Dodecene; (10) rt= 22.2 min 1,3-ethyl-dimethyl-benzene; (11) rt = 24.3 min 1-methyl-butyl-benzene; (12) rt=27.8 min 1,4-methyl-2(2-methyl-propyl)-benzene; (13) rt= 26.6 min 1-methyl-2-methylene-cyclohexane; (14) rt= 27.1 min 1-methyl-3-hexyl-benzene; (15) rt= 32.8 min-2,6-dimethyl-naphthalene; (16) rt=34.6 min tridecanol; (17) rt=35.5 min 3-heptadecene; (18) rt = 35.8 8-heptadecene; (19) rt= 36.9 min 1,6-dimethyl-cyclohexane; (20) rt= 37.0 min Z,Z 10,12-hexadecdienal; (21) rt= 40.9 min 1,2-dimethyl-cyclohexene; (22) rt=44.0 min-1,2,3-tertahydro-naphthalene; (23) rt= 50.0 min; Cyclohexyl-acetate; (24) rt=51.5 min Oleic acid; (25) rt= 53.4 min Decahydrobenzo-[b]-fluoranthene; (26) rt=57.0 min 9,12-octadecadienoic acid



Supplementary Figure 2: Concentration (g/kg) composition based on the calibration of FAME from the catalytic hydrothermal processing of sunflower oil at 350 °C (A) and (B) for HZSM-5 with linseed, soya bean, jatropha and palm oil at 350 °C.



Supplementary Figure 3: SEC overlay of the three chromatograms of oleic at 350 °C oleic acid with HZSM-5 and HTL sunflower oil HZSM-5 at the same temperature

Supporting table 1: Mass fraction yield of bio-crude and gas and aqueous phases from the hydrothermal processing of vegetable oils for 1h with different doped zeolite catalysts with an error of 3.0 %

Reaction conditions	bio-crude yield (%)	gaseous yield (%)	aqueous phase (%)
	Sunflower oil		
250 °C	74.0	0.0	26.0
300 °C	87.0	0.0	13.0
350 °C	86.0	3.8	10.2
350 °C HZSM-5	68.0	4.0	28.0
350 °C MoZSM-5	60.0	7.6	32.4
350 °C CoZSM-5	63.0	3.8	33.2
350 °C CrZSM-5	70.0	8.3	21.7
350 °C FeZSM-5	58.0	5.6	36.4
	Linseed oil		
250 °C	91.0	0.0	9.0
300 °C	99.0	0.0	1.0
350 °C	93.0	4.2	2.8
HZSM-5	81.0	4.2	14.8
	Soybean oil		
250 °C	90.0	0.0	10.0
300 °C	95.0	0.0	5.0
350 °C	90.6	3.8	5.6
HZSM-5	79.0	4.2	16.8
	Jatropha oil		
250 °C	89.0	2.7	8.3
300 °C	89.0	2.8	8.2
350 °C	93.0	4.2	2.8
HZSM-5	77.0	4.4	18.6
	Palm oil		
250 °C	89.0	0.0	11.0
300 °C	88.0	0.0	12.0
350 °C	90.0	4.2	5.8
HZSM-5	79.0	4.3	16.7
HTL oleic acid	97.0	0.0	3.0
HTL linoleic acid	92.0	4.4	3.6
HTL linolenic acid	93.0	4.2	2.8
HTL synthetic sunflower	86.0	4.4	9.6
HTL synthetic linseed	86.0	5.0	9.0
HTL synthetic jatropha	73.0	4.3	22.7
HTL oleic acid HZSM-5	53.0	4.5	42.5