POLITECNICO DI TORINO
Repository ISTITUZIONALE

Bio-Hydrocarbons through Catalytic Pyrolysis of Used Cooking Oils: towards sustainable jet and road fuels

(Article begins on next page)

02 May 2024

ATI 2015 - 70th Conference of the ATI Engineering Association

Bio-Hydrocarbons through Catalytic Pyrolysis of Used Cooking Oils: towards sustainable jet and road fuels

David Chiaramonti[a],*, Marco Buffi[a], Andrea Maria Rizzo[a], Matteo Prussi[a], Francesco Martelli[a]

[a]RE-CORD / CREAR, Dept.of Ind.Engineering, University of Florence, Viale Morgagni 40/44, Florence 50134, Italy.

Abstract

Vegetable Oil (VO) is today the most used feedstock for transport biofuel production by transesterification to biodiesel. Other commercial technologies for renewable fuels production are mainly based either on Fischer-Tropsch (FT) synthesis from coal, natural gas and possibly biomass, or hydro treating of vegetable oil (Hydrotreated Vegetable Oil, HVO): this also includes Hydrotreated Renewable Jet fuel, HRJ, Used Cooking Oil (UCO) is a highly sustainable feedstock (based on EC-RED scheme): it is therefore considered as a possible alternative to VOs for greening of air transport and, under proper circumstances, for reducing the feedstock cost component. However, the use of UCO is not trivial in reactors, as catalysts are sensitive to impurities and contaminations, which are typical of waste oils. Moreover, the chemical composition of UCO is variable regionally as well as seasonally, because the type of base-vegetable oils vary with Country and period of the year. In the framework of the ITAKA EU FP7 project, (catalytic) thermochemical conversion of UCO has been considered to obtain an intermediate biofuel suitable for upgrading by hydrotreating. The catalytic conversion of UCO and Fatty Acids were investigated in a 1.5 kg/h pilot unit. UCO, properly filtered and conditioned, was characterized, and then converted in bio-oil by means of thermal and catalytic reactionsunder controlled conditions. The type of catalyst and the reaction conditions, including several parameters such as temperature, reactor geometry, heating rate and residence time, were evaluated, and selected combinations were tested. The bio-oil was characterized in terms of main constituents and hydrocarbons content, and GC-MS and GC-FID analyses were used to qualitatively and quantitatively assess the composition of the fuel.

1. Introduction

Today the main use of traditional biofuels is blending them with traditional fossil fuel, in defined content, in order to stem the non-conventional properties of biofuels such as density, heat value, viscosity and O content[1]. The EU regulation promulgates a set of biofuel sustainability criteria to achieve the 2020 targets[2,3], but currently the oil price plays a significant role on their spreading [4]. In last years,

the interest is going towards the production of renewable hydrocarbons fuels to meet the fossil fuel properties for direct use in existing technologies[5].The only commercial process to convert biomass in green fuels consists on hydrotreating of vegetable oils and fats, a co-process of oil refineries, which is not only an opportunity but also a challenge for petroleum industry [6]. For its spreading, the main drawbacks are the availability of raw material and the large consumption of hydrogen during the process, which increases the production cost[7].However in aviation sector, where the fuel specifications play a significant role in terms of fuel quality, the HEFA (Hydroprocessed Esters and Fatty Acids) process is considered the most promising technology to produce drop-in blending renewable components for jet fuels [8].In this context, the ITAKA consortium[9] is developing a full value-chain in Europe to produce sustainable drop-in Synthetic Paraffinic Kerosene (SPK), in order to meet the economic, social and environmental issues at large scale, for testing it in existing logistic systems and in normal flight operations in Europe[10].

The scope of present work is based on the results from experimental activities obtained by RE-CORD group in the framework of ITAKA project, in particular from the thermochemical alternative process to hydrotreating. The selected process consists in the catalytic upgrading of pyrolysis vapours starting from used cooking oil as feedstock, in order to produce a fraction of bio-hydrocarbons from bio-oil collected.

Catalytic conversion of triglycerides-based materials for the production of biofuels was deeply investigated in literature and compared to hydrotreating [11, 12].Main goal consists on developing a process for deoxygenating the carboxylic group of fatty acids molecules, where reaction products are strongly affected by the catalyst type and reaction conditions [13]. This process works without using hydrogen for saving energy costs. Several catalysts were evaluated focusing the attention on final product composition [14–16], which can range from diesel like fractions to gasoline like fractions. Thus, four catalysts were selected and tested for this campaign. The choose of adopting used cooking oil as raw material is based both in the valorisation of a waste material, and primarily because this feedstock can rapidly deactivate the catalyst adopted in commercial hydrotreating [17], due to the high degree of randomness of their composition[18]. In this context the catalytic conversion is a promising alternative.

2. Materials and Methods

2.1. Experimental unit

The unit adopted is an intermediate pyrolysis unit [19], with the possibility to upgrade the pyrolysis vapours by means of a catalytic reactor. The unit is able to process up to 1.5 kg h-1of bioliquids such as animal fats, vegetable and used oils work adopted for ITAKA project. The feeding system consists in a heated injection system to reduce the oil viscosity. The thermal reactor is heated by electrical resistors of 12 kWe and capable of maintaining the reactive environment up to 550 °C. The reactor temperature is measured and controlled by means of a K type thermocouple place in the middle of the reactor. The catalytic reactor, properly heated by a dedicated resistor (3 kWth), is aimed to upgrade the pyrolysis vapours by means of a catalyst bed. During operation, a Nitrogen flow is flushed into thermal reactor at constant flow rate of 4 l min-1 for maintaining inert atmosphere. Condensation system consists of two water-cooled condensers connected in series and a water bubbler to remove the aerosol from non-condensable gases. The permanent gases are aspirated and discharged by a blower.

2.2. Test procedure

First, the experimental campaign was conducted at three different temperatures in the thermal reactor (450, 500 and 550 °C) without catalytic upgrading, in order to select the best yield in terms of bio-oil collected. Then, catalytic campaign was conducted at selected temperature both in thermal and catalytic

reactor, at fixed Weigh Hourly Space Velocity (WHSV) of 4 h-1. Four catalysts were selected in order to maximize the hydrocarbons fraction into bio-oil by means of data collected in literature [20]. No further information can be provided about the adopted catalysts due to licensing of process. The best catalytic performance, in terms of bio-oil yield and quality, is repeated by increasing the mass of the most performant catalyst, i.e. at WHSV of 2.5 h-1. Time of stream is approximately 90 minutes per test.

2.3. Determination of chemical classes with GC-MS and GC-FID

The composition of hydrocarbons, fatty acids and other compounds contained into bio-oil samples is determined using a GC-MS and a GC-FID apparatus of a gas chromatograph GC 2010 Plus (Shimadzu).Chemical species were first identified by means of GC-MS, comparing their mass spectra with the NIST library, and then quantified in mass by means of GC-FID internal standards.

3. Results

3.1. Feedstock

UCO adopted in this work was provided by SILO srl, a private company that is working on exhausted cooking oil and fats from several years, collecting the feedstock by means of contracts with private companies of the Florence district. Table 1 shows the analytical analysis on used cooking oil adopted, which was properly filtered at 1µm by means of industrial filtration system of SILO srl. The UCO was compared with a commercial sunflower oil in order to compare the most significant properties.

Table 1.Analytical analysis on feedstock.

Parameter	Unit	Method	Sunflower oil	UCO filtered at 1 µm
Density	kg/m^3	UNI EN ISO 3675	920	911
Kinematic Viscosity at 40 °C	mm^2/s	UNI EN ISO 3104	27.84	38.15
Acid value	$mg\ KOH/g$	UNI EN 14104	7.2	2.63
Free Fatty Acid	%	ISO 660	3.6	1.31
Water content	%	UNI EN ISO 8534	0.125	0.080
Total contamination	mg/kg	UNI EN 12662	206.3	256
C	%	ASTM D 5291	76.5	76.3
H	%	ASTM D 5291	11.3	11.7
N	%	ASTM D 5291	0.33	0.02
N	mg/kg	ASTM D 4629	116	137
O	%	Calculated	11.87	11.98
Calorific value, higher	kJ/kg	DIN 51900-2	39320	38910
Calorific value, lower	kJ/kg	Calculated	36922	36427

After filtration UCO presents similar characteristics to sunflower oil. Only the viscosity of UCO is slightly higher than sunflower oil (probably due to differences in fatty acid composition), while the water content and the contaminations were strongly reduced from the original batch.

3.2. Bio-oil quality and yield

Three preliminary tests were conducted without catalyst at 450, 500 and 550 °C in thermal reactor, for individuating the best performance in terms of bio-oil collected (i.e. higher liquid yield obtained). The test carried out at 500 °C was selected as reference, in terms of best liquid yield performance (i.e. 62.7 %wt) for next catalytic campaign. In Table 2 are reported the results on the experimental campaign, with the liquid yield obtained for each test and the quality of bio-oil produced.

Table 2.Analysis on bio-oil yield and quality for each test. Norms of analytical analysis are the same adopted in Table 1.

Parameters	Unit	No CAT	CAT n.1	CAT n.2	CAT n.3	CAT n.4
Feedstock		UCO	UCO	UCO	UCO	UCO
WHSV	*1/h*		4	4	4	4
Process temperature	*°C*	500	500	500	500	500
Liquid yield	*wt%*	62.70	63.64	54.55	33.74	61.72
Non-converted fraction	*wt%*	15	15	15	15	15
Permanent gas yield	*wt%*	22.3	21.36	30.45	51.26	23.38
C	*wt%*	76.75	76.10	76.03	77.90	78.17
H	*wt%*	11.45	11.10	11.65	10.10	11.48
N	*wt%*	0.02	0.03	0.08	0.07	0.03
O	*wt%*	11.98	12.77	12.25	11.93	10.33
Water content	*wt%*	0.89	0.77	1.18	8.36	1.61
Density	*kg/litre*	0.87	0.85	0.85	0.90	0.86
Acid value	-	117.73	74.10	61.97	20.45	80.07
Kinematic viscosity (40°C)	*cSt*	4.47	2.24	3.36	1.19	5.68
LHV	*MJ/kg*	36.82	37.79	39.57	36.48	37.46
HHV	*MJ/kg*	39.25	40.14	42.02	38.55	39.95

Bio-oils were collected in the range from 33.74 to 63.64 %wt (i.e. liquid yields), and the unconverted fraction (collected at the end of each test) was around 15 %wt of total feed (because catalytic effect acts on pyrolysis vapours). This led to estimate the permanent gas yield by difference, that was minimized in test with CAT n.1 (21.36 %wt) favouring the maximization of bio-oil collected. From CHNO analysis emerges that deoxygenation grade was lower than expected, but significant changes are observed in chemical composition by means of GC analysis in next paragraph. Water content is higher in test with CAT n.3, where the produced reaction water maybe is caused by the higher grade of cracking, which led the production of larger amount of permanent gases. Density is reduced, from the original feedstock, up to 0.85 kg l-1, and more significantly the viscosity values are reduced from 5.68 to 1.19 cSt, close to fossil fuel parameters. Acid value is strongly increased from the original feedstock due to FFAs content into bio-oil and other acidic compounds derived from cracking of triglycerides molecules. The catalytic effect is significant in all tests because the acidity was reduced, decreasing from 117.73 (test without catalyst) to 20.45 (test with CAT n.3). Finally the measured heat value is slightly higher than original feedstock despite the CHNO content, maybe caused by the non-uniformity and non-homogenous nature of bio-oil.

3.3. GC analysis on bio-oils

The identification and quantification of chemical species contained into bio-oil were carried out following the procedure in paragraph 2.3 and reported in Table 3. Essentially, this table shows the most significant chemical species as fuel, in particular the hydrocarbons fraction and FFAs produced for each test.

Table 3. Composition of bio-oil fractions analyzed in Table 2:results from GC-FID analysis.

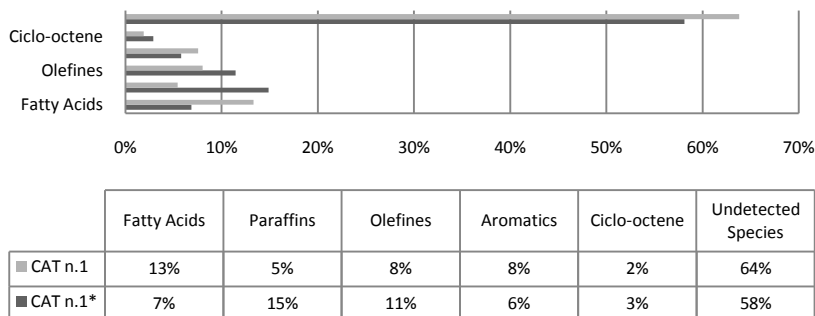| Parameter	Unit	NO CAT	CAT n.1	CAT n.2	CAT n.3	CAT n.4
FattyAcids	*wt%*	40%	13%	12%	3%	18%
Paraffins	*wt%*	3%	5%	3%	1%	1%
Olefines	*wt%*	6%	8%	7%	0%	3%
Aromatics	*wt%*	2%	8%	1%	4%	1%
Ciclo-octene	*wt%*	2%	2%	2%	0%	2%
Tot. Hydrocarbons	*wt%*	12%	23%	13%	5%	7%
Sum of Identified Species	*wt%*	52%	36%	25%	8%	25%
Undetected Species	*wt%*	48%	64%	75%	92%	75%

A large amount of unidentified classes such as oxygenated compounds (e.g. ketones, aldehydes and esters[13]), other free radicals from cracking reactions and polymerized products were not detectable from GC-FID library. According to this scheme, the interest goes towards the main classes of hydrocarbons such as paraffins, olefins and aromatics, and their distribution into each sample of bio-oil collected. Moreover, the FFAs content indicates the conversion grade obtained from the catalytic upgrading of vapours by means of the effect of catalyst, that favours secondary reactions (e.g., decarboxylation, decarbonylation, aromatization, cyclization, hydrogenation) according to scheme proposed by Idem at al [14] for the catalytic conversion of canola oil. From non-catalytic reference test, the FFAs content into bio-oil was 40 %wt that was strongly reduced after each catalytic test, in particular in test with CAT n.3 (i.e. 3 %wt) where the sum of undetected species reached the 92 %wt, maybe to high grade of cracking achieved that led the production of a large amount of undetectable radicals. Other catalytic tests show promising results, in particular CAT n.1 contains the 23 %wt of the sum of detected hydrocarbons, which is much higher than other tests. Except the test with CAT n.3, all tests indicate the presence of 2 %wt of ciclo-octene. From these results, the test with CAT n.1 was selected for next experiment with WHSV = 2.5 h^{-1}.

3.4. Test increasing catalyst mass

Catalyst mass was increased to obtain a WHSV = 2.5 h-1(i.e. test CAT.1*), maintaining the same temperature and parameters of previous tests. A measured liquid yield of 63.41 %wt- very similar to respective test with lower catalyst mass – was measured. Table 4 shows the results of GC analysis from the comparison between the two configurations.

Despite liquid yield was similar for both tests, increasing catalyst mass the FAs content reduced in favor of higher paraffinic and olefini cHC fraction, respectively from 5 to 15 %wt and from 8 to 11 %wt. The aromatic fraction reduced from 11 to 8 %wt, while the ciclo-octene content was slightly increased up to 3 %wt. It appears that higher aliphatics content into bio-oil was favored by decarboxylation and decarbonylation reactions occurred by longer residence times of the hot vapours into the catalyst reactor.

Table 4. Comparison between test with CAT n.1 with different mass of catalyst.

	Fatty Acids	Paraffins	Olefines	Aromatics	Ciclo-octene	Undetected Species
▪ CAT n.1	13%	5%	8%	8%	2%	64%
▪ CAT n.1*	7%	15%	11%	6%	3%	58%

4. Conclusions

This work investigated the catalytic upgrading of pyrolysis vapours produced by the thermochemical conversion of used cooking oil. Catalytic conversion through pyrolysis of UCO was performed at 500°C with 4 different catalysts (WHSV = 4 1 h-1). The best result (CAT n.1 test) gave 63.6 %wt of bio-oil, with slightly lower Oxygen content, but comparable results with diesel fuel specification in terms of density, viscosity and heat value. Increasing catalyst mass (WHSV = 2.5 1 h-1), there were no significant changes in terms of bio-oil yield, but larger fractions of hydrocarbons classes were detected (from 24 to 35%wt) by means of GC-MS/FID analysis. Separation of hydrocarbons needs further studies.

Acknowledgements

References

[1]   I. Barabás, I. Todoru, Utilization of Biodiesel-Diesel-Ethanol Blends in CI Engine, in: G. Montero (Ed.), Biodiesel-Qual. Emiss. By-Products, InTech, 2011: p. 21. http://www.intechopen.com/books/biodiesel-quality-emissions-and-by-products/utilization-of- biodiesel-diesel-ethanol-blends-in-ci-engine.

[2]   S. Afionis, L.C. Stringer, European Union leadership in biofuels regulation: Europe as a normative power?, J. Clean. Prod. 32 (2012) 114–123. doi:10.1016/j.jclepro.2012.03.034.

[3]   L. German, G. Schoneveld, A review of social sustainability considerations among EU-approved voluntary schemes for biofuels, with implications for rural livelihoods, Energy Policy. 51 (2012) 765–778. doi:10.1016/j.enpol.2012.09.022.

[4]   G.R. Timilsina, S. Mevel, A. Shrestha, Oil price, biofuels and food supply, Energy Policy. 39 (2011) 8098–8105. doi:10.1016/j.enpol.2011.10.004.

[5]   G. Knothe, Biodiesel and renewable diesel: A comparison, Prog. Energy Combust. Sci. 36 (2010) 364–373. doi:10.1016/j.pecs.2009.11.004.

[6]   S. Chen, Green Oil Production by Hydroprocessing, 2012 (2012) 43–55.

[7]   R. Sotelo-Boyás, F. Trejo-Zárraga, F. de J. Hernández-Loyo, Hydroconversion of Triglycerides into Green Liquid Fuels, in: InTech, 2012: p. 30. doi:http://dx.doi.org/10.5772/48710.

[8]   E4tech (UK) Ltd, Sustainable Aviation Fuels - Potential for the UK aviation industry, 2014.

[9]   EU FP7 ITAKA, EU FP7 Grant Agreem. No. 308807. (2012). http://www.itaka-project.eu.

[10]   D. Chiaramonti, M. Prussi, M. Buffi, D. Tacconi, Sustainable bio kerosene: Process routes and industrial demonstration activities in aviation biofuels, Appl. Energy. 136 (2014) 767–774. doi:10.1016/j.apenergy.2014.08.065.

[11]   V. Teixeira, L.A. Sousa, The Role of Catalysis for the Sustainable Production of Bio-fuels and Bio-chemicals, Elsevier, 2013. doi:10.1016/B978-0-444-56330-9.00003-6.

[12]   a. V. Lavrenov, E.N. Bogdanets, Y. a. Chumachenko, V. a. Likholobov, Catalytic processes for the production of hydrocarbon biofuels from oil and fatty raw materials: Contemporary approaches, Catal. Ind. 3 (2011) 250–259. doi:10.1134/S2070050411030044.

[13]   K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals., Bioresour. Technol. 98 (2007) 2351–68. doi:10.1016/j.biortech.2006.10.025.

[14]   R.O. Idem, S.P.R. Katikaneni, N.N. Bakhshi, Catalytic conversion of canola oil to fuels and chemicals: roles of catalyst acidity, basicity and shape selectivity on product distribution, Fuel Process. Technol. 51 (1997) 101–125. doi:10.1016/S0378-3820(96)01085-5.

[15]   L. Dandik, H.A. Aksoy, Effect of catalyst on the pyrolysis of used oil carried out in a fractionating pyrolysis reactor, Renew. Energy. 16 (1999) 1007–1010. doi:http://dx.doi.org/10.1016/S0960-1481(98)00355-3.

[16]   E. Vonghia, D.G.B. Boocock, S.K. Konar, A. Leung, Pathways for the Deoxygenation of Triglycerides to Aliphatic Hydrocarbons over Activated Alumina, Energy & Fuels. 9 (1995) 1090–1096. doi:10.1021/ef00054a024.

[17]   S. De, R. Luque, Upgrading of waste oils into transportation fuels using hydrotreating technologies, Biofuel Res. J. 4. 4 (2014) 107–109.

[18]   G. Knothe, K.R. Steidley, A comparison of used cooking oils: a very heterogeneous feedstock for biodiesel., Bioresour. Technol. 100 (2009) 5796–801. doi:10.1016/j.biortech.2008.11.064.

[19]   A.M. Rizzo, M. Prussi, L. Bettucci, I.M. Libelli, D. Chiaramonti, Characterization of microalga Chlorella as a fuel and its thermogravimetric behavior, Appl. Energy. 102 (2013) 24–31. doi:10.1016/j.apenergy.2012.08.039.

[20]   M. Buffi, A.M. Rizzo, D. Chiaramonti, A review of renewable-jet fuel from thermo-chemical conversion of vegetable and used cooking oil, in: Pyro2014 proceedings, 2014.
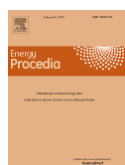
Biography

Eng. David Chiaramonti, PhD: President of RE-CORD Consortium. His main scientific interest is on the production and the use of biofuels, either liquid, gaseous or solid. His research work covers thermochemical biomass conversion processes as well as liquid biofuel production and use. Member of ISES-Italia, IEA-Bioenergy (Task 39), ISAF, ecc.