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Research paper

Bio-hydrocarbons through catalytic pyrolysis of used cooking oils and fatty acids for sustainable jet and road fuel production

David Chiaramonti*, Marco Buffi, Andrea Maria Rizzo, Giulia Lotti, Matteo Prussi

RE-CORD and CREAR, Industrial Engineering Department, University of Florence, Viale Morgagni 40, 50134 Florence Italy

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ABSTRACT

Used Cooking Oil (UCO) and pure Fatty Acids (FAs) derived from food processing represent sustainable feedstocks for biofuel production. The catalytic and non-catalytic pyrolysis of these residual oils is a possible pathway to advanced biofuel production, alternative to catalytic hydrotreatment, already commercially deployed in large-scale installations. The present work first carried out a literature review of previous research works in the field, which provided the key information to the following implementation of a pilot-scale dedicated experimental work aimed at producing bio-hydrocarbons from residual vegetable oils, with a special focus on paraffinic fuels. Based on the literature survey, 4 different catalysts were selected for the experimental investigation. Catalytic and non-catalytic pyrolysis of UCO was initially carried out in 1.5 kg h^{-1} (max) feed pilot unit, operated at 500 °C, with the catalytic reactor working at 4 and 2.5 h^{-1} Weight Hourly Space Velocity (WHSV). Liquid yields and corresponding hydrocarbon fractions were investigated: these initial results suggested to extend the study to catalytic pyrolysis of pure FAs. At $T = 500$ °C and with activated carbons as catalyst, the total observed hydrocarbon yield mass fraction on UCO and FA increased from 23% (UWHSV $= 4$ h^{-1}) to 35% (UCO, WHSV $= 2.5$ h^{-1}) and finally to 40% (FA, WHSV $= 2.5$ h^{-1}). A slight reduction in the overall liquid yield mass fraction was also observed in this last experiment with FAs (from 63% to ≈49%). Even if the current work on the pilot pyrolyser did not aim at investigating energy and process optimization, including yield maximization and catalyst lifetime, experimental results indicated that catalytic pyrolysis could be a promising way for industrial production of hydrocarbons from low quality lipid-based materials (as it is the case of UCOs) and without requiring hydrogen for catalytic hydrotreatment.

1. Introduction

Developing new routes to sustainable biofuel production is today a major R&D effort carried out worldwide. Several pathways addressing different types of feedstock have been and are currently under development. Catalytic pyrolysis is a possible new route, alternative to hydroprocessing of lipids, and able to address residual and irregularly (in time and quality) contaminated lipids, such as used cooking oils. The present work aims at studying this biofuel chain, placing this in the wider context of biofuel production and providing quantitative data from a specific experimental investigation.

Major processes routes and technologies towards Advanced Biofuel production have been summarised by several authors [1–3]: however, in the aviation field, biokerosene is today almost completely produced through the HVO chain. Aviation worldwide consumes around 220 Mt y^{-1} of commercial jet fuel (Jet-A1): air transport's contribution to climate change represents 2% of man-made CO_2 emissions, which could reach 3% by 2050, according to updated figures from the Intergovernmental Panel on Climate Change (IPCC) [4]. In Europe, while diesel demand achieved ~270 Mt y^{-1} and gasoline ~80 Mt y^{-1} (for a total of ~350 Mt y^{-1}), kerosene demand reached ~54 Mt y^{-1} in 2014. However, even if the major market volume potential for biofuels is still represented by road transports, aviation is the only sector that continued to grow considerably during the period 2008–2012 and maintained a rather constant level of consumption, despite the economic crisis that affected the major economies of the world. This fact, together with the very limited options existing for greening aviation, makes the target of developing sustainable aviation biofuels particularly attractive: nevertheless, technical issues and economic competitiveness still represent real challenges [5]. Today the lipid-based

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* Corresponding author.
E-mail address: david.chiaramonti@unifi.it (D. Chiaramonti).

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route through HVO/HEFA to paraffinic fuels for aviation production is probably the only one that achieved full technical and commercial scale (which obviously includes ASTM D7566 certification), while economic sustainability has not yet been reached. The EU project ITAKA is investigating technical and economic issue of HVO to biokerosene at full scale (including logistics, distribution, chain of custody, and transatlantic and EU passenger flights) [6]. Various other R&D and demonstration project are exploring other possible paths, such as the lignin-to-jet (EC FP7 Biorefly project by Biochemtex [7], alcohol-to-jet (BFSJ project by Swedish Biofuels [8]), or sugar-to-jet [9], with the last one that achieved ASTM certification.

1.1. *Pyrolysis of lipids for hydrocarbon production*

As indicated in Fig. 1, today the main production pathway of hydrocarbon biofuels from biomass is represented by the hydrotreatment (i.e. hydroprocessing and isomerization) of vegetable oils and lipids. The process initially removes the oxygen from the pretreated feed, separating CO_2 and water from a stream of diesel range waxy paraffins. Then a selective hydrocracking is carried out, generating a mixture of light, diesel and aviation fuels. Since the typical carbon number of diesel, Jet and naphtha/gasoline is 12–20, 10–15, and 4–12 respectively, the influence of the feedstock composition (in terms of fatty acids/triglycerides) is relevant to determine the carbon-length product distribution. The process requires significant amount of hydrogen and use expensive catalysts: the sensitivity of these catalysts to impurities is a critical element, in particular when feeding residual vegetable oils and UCO. Therefore, strict acceptance limits and quality standards are applied to the feedstock at the inlet gate, in order to avoid poisoning and de-activation of catalysts.

Pyrolysis could be effectively applied to lipids and fatty acids to remove the oxygen and generate hydrocarbons. The potential advantage of pyrolysis versus hydroprocessing relies in the fact that the process does not requires hydrogen and catalysts, or alternatively it can be run with low-cost catalysts, thus more tolerant to irregularly contaminated feed as UCO. Moreover, pyrolysis can be better downscaled than hydroprocessing, and thus it could be implemented at smaller scale in decentralised unit (especially targeting road transport fuels), placed close to the collection points of residual oils and well integrated in a local circular economy scheme. Pyrolysis of lipids could also be seen as a first step before hydroprocessing, able to deliver an already largely deoxygenated product to final upgrading steps. Various authors previously investigated pyrolysis of triglycerides and fatty acids, implementing the process in different ways. Selected previous studies on the subject are presented in the following section, addressing reaction mechanisms as well as catalytic and non-catalytic thermochemical conversion, in order to derive essential information to design our experimental work.

Reaction mechanisms in pyrolysis of lipids - Thermal cracking of vegetable oils was studied by Chang and Wang [10], that proposed a first scheme of 16 types of reaction for the triglyceride decomposition. The cleavage of the triglycerides molecules originates a mixture of hydrocarbons of smaller chains and oxygenated compounds, such as alkanes, alkenes, alkadienes, aromatics, aldehydes, ketones, and carboxylic acids. Teixeira and Sousa [11] proposed a two steps cracking mechanism: first (primary cracking), acid species (mainly carboxylic acids) are formed during the thermal decomposition of triglycerides by breakdown of C—O bonds of the carboxylic group, then (secondary cracking) the products from the first reaction are converted into shorter chain length organic compounds, including saturated and/or unsaturated hydrocarbons. The type of catalysts is selective to secondary reactions: for instance, zeolites favour the formation of aromatics compounds. The effect of primary cracking on saturated molecules of triglycerides was studied by Alencar et al. [12]. Basically this pathway follows the Rice free radical theory, modified by Kossiakoff, and referred as RK theory. Schwab et al. [13] investigated the pyrolysis of soybean oil, proposing a mechanism which considered the presence of unsaturated fatty acids into triglycerides molecules. In this case, the presence of unsaturation enhances the cleavage in proximity of double bonds (i.e. at α, β position of C═C) of fatty acids, leading to the formation of C5 to C10 alkanes. A detailed model of the reaction mechanism of canola oil was proposed by the Idem et al. [14], who carried out an experimental investigation of catalytic pyrolysis to study the reaction scheme, including the polymerization reactions. This scheme considers both saturated and unsaturated fatty acids, as well as the decomposition of the heavy oxygenated compounds (formed after polymerization) by different routes. Initial decomposition of triglycerides takes place with cleavage of C—O bonds (generating fatty acids and acrolein as intermediates), or C—C bond at position β (full carboxylic-group removal) leading to the formation of C═C bond, due to absence of free Hydrogen. However, the cleavage in proximity of C═C bond of the unsaturated fatty acid chains can occur simultaneously. These studies showed the complexity of pyrolysis reactions and the wide variety of products formed from the only cracking of triglycerides molecules. Given the difficulties to understand a well-defined reaction mechanism, Zhenyi et al. [15] studied pyrolysis mechanism of triglycerides focusing on thermal degradation of triolein, selected as reference structure for vegetable oils. They showed that cleavage of C—O bond takes place at the temperature of about 288 °C while the C—C bond at β position occurs at about

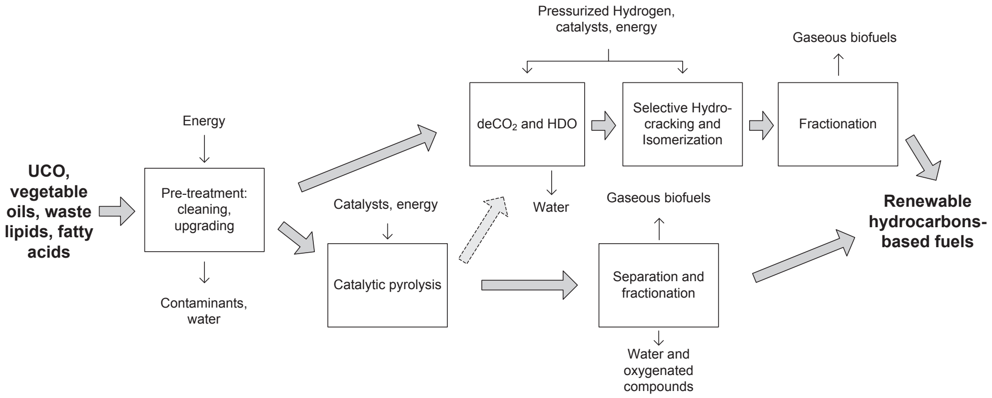

Fig. 1. HVO/HEFA versus thermochemical treatment of lipids.

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