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Research article

Integration of hydroprocessing modeling of bio-liquids into flowsheeting design tools for biofuels production

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ABSTRACT

Aim of this paper is to present an engineering tool for the design and modeling of the upgrading of three biomass derived liquids (bio-oil, vegetable oil and algal oil) through hydrotreating process for the production of advanced biofuels. For each case, the appropriate approach was followed regarding the model compound selection for each bio-feedstock, the main reactor modeling, the products separation and purification and the make-up hydrogen production. Simulation runs were performed in ASPEN Plus™ and revealed the importance for make-up H_2 production from recovered light gases and external fuel such as natural gas (the heat content on LHV basis if the inlet natural gas is 7.4% of the produced fuel in the jatropha oil case), showing also the beneficial impact of a good catalyst. The energy balance calculations showed that the most energy demanding components are the air compressor before reformer and make-up H_2 compressor at the hydrogen production plant. The assumption of a chemical equilibrium can be regarded as a well-fitting and valid approach for the process design. The representation of bio-liquid by a model compound (i.e. palmitic acid in case of algal oil) may result in good estimations in terms of mass (0.845 $kg_{G\text{-}Diesel}/kg_{algal\text{-}oil}$ product yield) and heat balance of the total process (94.9% thermal efficiency) but all the detected fatty acid is suggested be taken into account for a more detailed analysis.

1. Introduction

The interest for biofuel production (mainly bioethanol and biodiesel) has been increased significantly the last decades. In 2011, the worldwide production of bioethanol was > 1600 PJ whereas the biodiesel production exceeded the 830 PJ [1]. There are several routes for biomass transformation into liquid fuels, depending on the biomass feedstock properties and the final product (see Fig. 1).

Bio-oil production through fast pyrolysis is a rapidly developing technology. Its commercial implementation is very close to market deployment even though the bio-oil upgrading to added value transportation fuels is at research level yet. So far, there are pyrolysis plants at commercial scale in various countries such as USA, Canada, Finland, Malaysia, the Netherlands, etc. with a capacity ranging from 1670 to 21,000 kg/h [2–4] and new facilities are under development [5]. The main advantages of pyrolysis technology is the exploitation of any kind of lignocellulosic biomass, the high product yield (up to 75%) [6,7], while the produced bio-oil (biocrude) is relatively stable, compatible with existing refineries and able to be converted into advanced biofuels.

More than 12% of the total vegetable oil production is used for biofuel (i.e. biodiesel) production [1]. Vegetable oils, waste cooking oils and animal fats react with methanol/ethanol producing biodiesel, an attractive alternative fuel of fossil derived diesel oil, which is free of sulfur, has reduced biodegradability non-toxic features [8,9]. Among the abovementioned feedstocks, vegetables oils dominate because of their high heating value and their ready availability [10]. However the alternative route of vegetable oil conversion into an applicable liquid fuel through hydroprocessing has attracted the industrial interest of various companies the last years such as Neste, ENI, Haldor Topsoe and Axens IFP [11,12]. For instance, NEXBTL technology developed by Neste is an advanced hydrotreating technology for renewable diesel production from vegetable oils and waste animal fat at commercial scale [12,13].

Algae, one of the oldest life-forms, belongs to the third generation biofuels (together with microbes) and is considered as a viable energy resource that is not related to the major drawbacks associated with first and second-generation biofuels (i.e. competition with edible crops and land use) [14]. The main advantage of this biofuel is the high growth rates and the lipids accumulation (20%–80% of dry weight) higher than vegetable oil crops (up to 5% of dry weight) [15–17]. Among other

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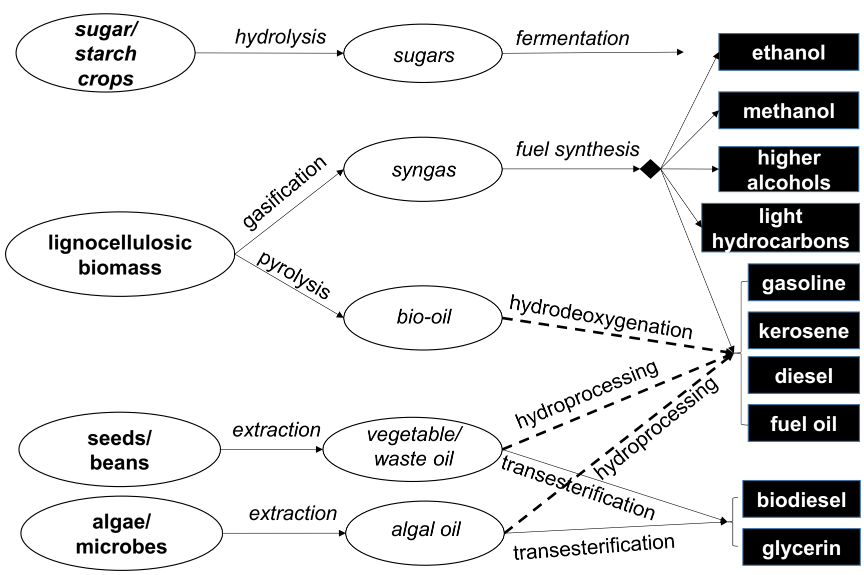

Fig. 1. Process pathways for biomass valorization (with dashed line the processes that are investigated in this study).

benefits of microalgae cultivation in comparison to conventional land farms are their less water demand, their more cost-effective farming, their less nitrous oxides emissions and higher CO_2 mitigation [18].

Biodiesel, which is a mixture of fatty acid methyl esters (FAME) is used only as additive to petro-diesel and is not expected to completely replace it, mainly due to its composition (high O content). On the hand, green diesel (G-Diesel), which is a mixture of hydrocarbons is produced via hydroprocessing has the potential substitute the petroleum based fuels. At the same wavelength, the strict specifications the aviation fuels need to confront with [19–21], designate that the bio-liquids which are mainly triglyceride esters such vegetable oils and algal oil, must undergo catalytic hydroprocessing in order to be converted into appropriate for aviation engine advanced fuels.

The major catalytic reactions that are involved in the bio-liquids upgrading using hydrogen, are hydrodeoxygenation (HDO), hydrodecarboxylation (HDC) and catalytic isomerization. During HDO reactions, oxygen in the form of oxygenate compounds is removed as H_2O, while in hydrodecarboxylation/hydrodecarbonylation, oxygen is removed in the form either CO or CO_2 (see Fig. 2). HDO is the main and more important reaction which takes place during hydroprocessing of the bio-based liquids. The conversion rate of HDO is favored at high pressures and at temperatures around to 300–400 °C [22,23].

Limited studies dedicated to hydroprocessing modeling and the design of such bio-derived liquids upgrading through hydrogen can be found in the literature. Most of them have been performed by the Department of Energy ([26] for vegetable oil, [27,28] for algal oil, [26,29] for bio-oil). Indicatively, Terry Marker performed a feasibility study on some of these oils (vegetable and pyrolysis oil) to evaluate the potential use of them in an oil refinery. It is revealed that hydrotreating processes on both bio-feedstocks have increasing prospects of economic viability [26]. These scarce works are partially based on process simulations performed in ASPEN Plus, but the modeling of the basic hydroprocessing steps was developed based on yields from relevant experiments.

Bio-based industries and traditional refineries plan to install hydroprocessing units in their production line, able to operate with diverse bio-derived feedstocks, for their effectively upgrading into fuels able to substitute the corresponding conventional ones (gasoline, diesel, jet fuel). So far, the modeling presentation of an integrated hydrotreating process of bio-based feedstocks that focuses on the influence of the main operation parameters (such as feedstock composition, pressure, temperature and H_2/oil ratio, etc.) and the make-up H_2 production route absences from the literature. The scope of this paper is to present an engineering tool for the design of large scale integrated hydroprocessing units of various biomass derived liquid, taking into account 1) the approach that should be adopted for the feedstock and

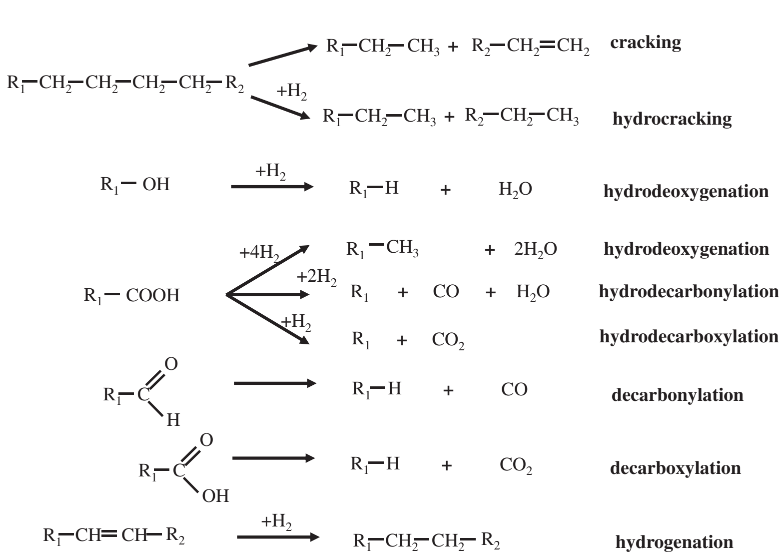

Fig. 2. Reactions occurred during catalytic hydroprocessing of bio-based liquids (R_i: saturated alkyl group, R′: unsaturated alkyl group) [24,25].