Applied Energy 149 (2015) 404–414

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Decarbonisation of olefin processes using biomass pyrolysis oil

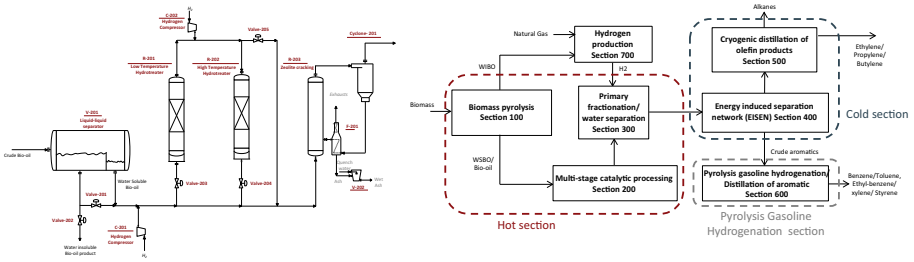
M. Sharifzadeh [a,*], L. Wang [b], N. Shah [a]

[a] Centre for Process Systems Engineering (CPSE), Department of Chemical Engineering, Imperial College London, United Kingdom
[b] Centre for Environmental Policy, Imperial College London, United Kingdom

HIGHLIGHTS

- Decarbonization of olefin processes using biomass pyrolysis oil was proposed.
- The decarbonization is based on integrated catalytic processing of bio-oil.
- The retrofitted process features significant economic and environmental advantages.

GRAPHICAL ABSTRACT



Decarbonisation of conventional olefin processes by integrated catalytic processing of biomass pyrolysis oil

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 8 February 2015
Accepted 17 March 2015
Available online xxxx

Keywords:
Decarbonisation
Olefins
Biomass pyrolysis oil
Techno-economics
Life cycle assessment

ABSTRACT

An imperative step toward decarbonisation of current industrial processes is to substitute their petroleum-derived feedstocks with biomass and biomass-derived feedstocks. For decarbonisation of the petrochemical industry, integrated catalytic processing of biomass pyrolysis oil (also known as bio-oil) is an enabling technology. This is because, under certain conditions, the reaction products form a mixture consisting of olefins and aromatics, which are very similar to the products of naphtha hydrocracking in the conventional olefin processes. These synergies suggest that the catalytic bio-oil upgrading reactors can be seamlessly integrated to the subsequent separation network with minimal retrofitting costs. In addition, the integrated catalytic processing provides a high degree of flexibility for optimization of different products in response to market fluctuations. With the aim of assessing the techno-economic viability of this pathway, five scenarios in which different fractions of bio-oil (water soluble/water insoluble) were processed with different degrees of hydrogenation were studied in the present research. The results showed that such a retrofit is not only economically viable, but also provides a high degree of flexibility to the process, and contributes to decarbonisation of olefin infrastructures. Up to 44% reductions in greenhouse gas emissions were observed in several scenarios. In addition, it was shown that hydrogen prices lower than 6 $/kg will result in bio-based chemicals which are cheaper than equivalent petrochemicals. Alternatively, for higher hydrogen prices, it is possible to reform the water insoluble phase of bio-oil and produce bio-based chemicals, cheaper than petrochemical equivalents.

1. Introduction

Amongst major energy-users and GHG emitters, industrial processes are responsible for one third of the total worldwide energy consumptions and associated emissions. In addition, many industrial processes consume energy products as their feedstock. The main challenge is that industrial processes have long life cycles, in the order of decades, and the number of new processes which are being built is significantly smaller than the number of processes which are currently in use. These observations suggest that an important pathway toward decarbonisation of industrial

* Corresponding author. Tel.: +44 (0)7517853422.
E-mail address: mahdi@imperial.ac.uk (M. Sharifzadeh).

http://dx.doi.org/10.1016/j.apenergy.2015.03.081
0306-2619/

processes is through retrofitting these processes. In particular, substituting petroleum-derived feedstocks with renewable feedstocks has substantial potential for mitigating the greenhouse gas (GHG) emissions and protecting the environment. However, most of the research in the field is focused on developing new processes which are subject to a high degree of uncertainty in sale-up and commercialization. The present paper explores the opportunity for substituting the naphtha feedstock in a conventional olefin process with biomass pyrolysis oil (also known as bio-oil). The research significance is due to the fact that the olefin process is highly energy-intensive and its products are essential for polymer production. Therefore, alternative production pathways have been under scrutiny [1–5].

The pathways for producing liquid fuels from biomass include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation, and gasification [6], among which biomass pyrolysis provides the cheapest pathway toward renewable chemicals and fuel [7]. In principle, pyrolysis is the precursor of biomass gasification or combustion and refers to set of reactions occurring when biomass is heated in the absence of oxygen [6]. Nevertheless our knowledge of biomass pyrolysis is limited; Mettler et al. [8] identified ten fundamental challenges in biomass pyrolysis with an emphasis on understanding the chemistry of conversion pathways, heat transfer phenomena and particle shrinkage. The diverse array of research into biomass pyrolysis include advanced analytical chemistry methods for bio-oil characterization [9–11], developing kinetic models for the pyrolysis reactions [12], computational fluid dynamic studies [13], design of new reactors [14], developing new heating methods such as microwave assisted pyrolysis [15,16], optimizing the bio-oil yield and process configuration [17], developing various bio-oil upgrading methods [18,19], process intensification [20], techno-economic analysis [21,22], environmental assessment [23,24], and enterprise-wide and supply chain optimization [25–27]. A recent review of the research into biomass fast pyrolysis has been published by Meier et al. [28].

Despite various economic incentives, biofuel commercialization poses an important challenge; the effluent of pyrolysis reactions, called bio-oil features undesirable properties such as chemical instability, high acidity, low heating value and immiscibility with petroleum-derived fuels. Therefore, upgrading bio-oil poses an important challenge. The conventional technologies for upgrading bio-oil include aqueous processing, hydrodeoxygenation (HYD), and zeolite cracking. The most common upgrading method is hydrotreatment upgrading of bio-oil which was originally inspired by similar processes for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) in petroleum refineries [29]. However, the amount of heteroatoms (*i.e.*, oxygen) is an order of magnitude larger in the case of bio-oil. The implication of high oxygen content is excess coke formation. The resolution is multistage treatment in which firstly the bio-oil is stabilized in a low temperature reactor and then a deeper hydrodeoxygenation is accomplished in the second stage reactor at a higher temperature [30]. Here, we differentiate between *char* and *coke*. The former is a by-product of biomass pyrolysis, and is favored at relatively low temperature and low heating rate [31]. By contrast, the latter refers to the carbon atoms deposited on the catalysts surface of the upgrading reactors and is favored at low hydrogen partial pressures, [7,32].

While hydrotreating does not alter the boiling range of hydrocarbons significantly, zeolite cracking is an efficient pathway to produce large qualities of light products by depolymerisation of heavy oligomers [33]. The challenge is that the coking can be so severe that a fixed bed reactor may become plugged quickly. Pretreatment using multi-stage hydrodeoxygenation can mitigate the problem [34]. In addition, fluidized bed reactors have the advantage that the coked catalyst can be regenerated and recycled to the reactor. Aqueous processing (also known as hydrothermal treatment) refers to a water-rich scenario at temperature above 200 °C, and a pressure sufficiently high to maintain the water at the near supercritical or supercritical state. It is widely observed that at these conditions water exhibits distinct processing advantages such as enhanced and tunable properties (*e.g.* solubility, solvent polarity, transport properties), and ease of solvent removal [35]. Other advantages of this technology include avoiding phase change and parasitic energy losses due to high pressure processing, versatile chemistry to existing chemical and fuel infrastructure, enhanced reaction rates [36], and minimal hydrogen consumption [37]. However, the engineering challenges include unknown reaction mechanisms, uncharacterized reaction pathways and severe processing conditions that the catalysts may not withstand.

Techno-economic performance of the fast pyrolysis pathway has been the focus of intensive research. Initial evaluations were made by research institutes. For example a detailed techno-economic analysis was conducted by Jones et al. [38] at Pacific North West National Laboratory (PNNL). The process consisted of a circulating fluidized bed pyrolysis reactor followed by two-stage hydrogenation reactors. Then, in a sequence of distillation columns, the stabilized bio-oil was resolved into biofuels with similar properties to naphtha and diesel. The heavy fraction was sent to a hydrocracker before recycling to the distillation columns. In this process, the hydrogen required for bio-oil hydrogenation and hydrocracking was produced through reforming natural gas. A technoeconomic comparison was made to the scenario where the process was co-located with a conventional refinery and the hydrogen was imported. Since the economy of bio-oil production is a strong function of hydrogen prices, Wright et al. [39] proposed a process in which, a fraction of bio-oil was partially reformed to produce the required hydrogen for upgrading the remaining bio-oil. They concluded that producing hydrogen from bio-oil itself is more profitable compared to purchasing hydrogen. Recently, Shemfe et al. [40] studied the technoeconomic performance of fast pyrolysis for cogeneration of biofuel and electricity power. A merit of this study was incorporation of rate-based chemical reactions for modelling the hydroprocessing section. In parallel, technoeconomic analysis of producing commodity products through catalytic upgrading the bio-oil has been the focus of several researchers. Vispute et al. [7] showed that the annual economic potential (EP) of this pathway strongly depends on the hydrogen price. Later, Brown et al. [41] conducted a more detailed techno-economic analysis. They identified the biomass pyrolysis yield as an important factor in economic viability of this technology. Later, Zhang et al. [42] compared the biofuel pathway with the commodity chemical pathway. They concluded that a scenario where the required hydrogen is produced through natural gas reforming is the most economic option. All the aforementioned studies applied simplified process flowsheeting sufficient for calculating overall mass balances and did not include the sophisticated separation network required for resolving the highly complex olefin-aromatic mixture into marketable high purity products. The present research extends the previous studies by adapting the catalytic upgrading technology for retrofitting existing olefin process and evaluates the opportunity for decarbonisation of olefin industries through substitution of their conventional petroleum feedstocks (e.g., naphtha) using the renewable pyrolysis bio-oil. The present analysis is comprehensive and includes technoeconomic as well as environmental life cycle assessments.

Recently, Vispute et al. [7] developed a reaction network for upgrading bio-oil which combines the advantages of all three aforementioned technologies in order to produce an array of olefin and aromatic products as a fungible feedstocks for existing refinery