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Aromatization of propane: Techno-economic analysis by multiscale "kinetics-to-process" simulation

Michele Corbetta[a], Flavio Manenti[a,*], Carlo Pirola[b],
Mark V. Tsodikov[c], Andrey V. Chistyakov[c]

[a] *Politecnico di Milano, Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Piazza Leonardo da Vinci, 32, 20133 Milano, Italy*
[b] *Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi, 19, 20133 Milano, Italy*
[c] *A.V.Topchiev Institute of Petrochemical Synthesis, Leninskiy prospect, 29, Moscow 119991, Russian Federation*

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ABSTRACT

This paper addresses the techno-economic analysis of the propane aromatization process, by adopting a novel kinetics-to-process approach. The recent interest in this technological route derives from the development of new third generation biorefinery concepts, in which, algal oil is subjected to catalytic hydrodeoxygenation processes for the production of (Hydrotreated Renewable Jet) HRJ fuels. Beside biofuels, co-production of large amounts of propane is observed, which can be upgraded by a catalytic conversion to aromatics on zeolites. Kinetic studies of propane aromatization over H-ZSM-5 zeolite in a wide range of conversions are reported in the literature. Based on these results, a general kinetic model of propane aromatization has been developed. The revised kinetic scheme is then embedded in a process simulation, performed with the commercial code SimSci PRO/II by Schneider Electric. Basing on the process simulation and on available price assessments, a techno-economic analysis has been performed to show limits as well as potentialities of the proposed layout.

1. Introduction

The recent interest in third generation biorefineries results in an increased attention on correlated processes for the valorization of by-/co-products, which are the perquisite for a zero-waste and economic sustainable plant.

Focusing the attention on oleaginous biomass sources (e.g., microalgae), two main technological routes are adopted for the conversion of raw bio-oil to biofuels. The first one that had been developed is the transesterification to biodiesel, which is defined as the mono-alkyl esters of fatty acids (FAME) derived from triglycerides. Transesterification with an alcohol, such as methanol, occurs under mild conditions in the presence of a base catalyst and co-produces low-value glycerol, which can be subjected to aqueous-phase-reforming to produce hydrogen. Recent works show the possibility to pre-treat raw oil (broadly composed by a triglyceride mixture) with a catalytic deacidification step in order to lower the free-fatty-acids (FFA) content and to avoid soap formation in the subsequent transesterification process, starting either from waste animal fat (Bianchi et al., 2009) or raw sunflower oil (Pirola et al., 2014). The second technological route consists in a hydrodeoxygenation at high temperature and pressure in the presence of a catalyst, with the production of drop-in renewable (green) diesel and hydrotreated renewable jet (HRJ) fuels. Hydroprocessing is employed in conventional refinery processes to firstly deoxygenate and remove undesirable materials including nitrogen, sulphur and residual metals and break down carbon chain lengths. Similarly, the biomass synthetic jet fuel production process involves removing oxygen molecules and other undesirable materials from triglycerides through hydrotreatment, and a subsequent selective hydrocracking/rearrangement of the atomic structure to yield lighter hydrocarbons suitable for aviation (Jet A-1: C8–C16) (Blakey et al., 2011). These catalytic processes determine the cracking of triglycerides, saturation of double bonds, heteroatoms rejection and isomerization. The main difference between biodiesel and green diesel consists in their chemical characterization. Green diesel is a drop-in fuel with a chemical structure similar to the petro-derived diesel irrespective of the feedstock and without oxygen content, which is not true for biodiesel (Knothe, 2010). HRJ fuel is substantially composed by a pool of long chain paraffins free from aromatics compounds. As a consequence, HRJ fuel meets the world jet fuel specifications (ExxonMobil Aviation, 2005) for the threshold value of 25 vol% of aromatics in the Jet A-1 category.

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* Corresponding author. Tel.: +39 0 2 2399 3273; fax: +39 0 2 2399 3280.
E-mail address: flavio.manenti@polimi.it (F. Manenti).

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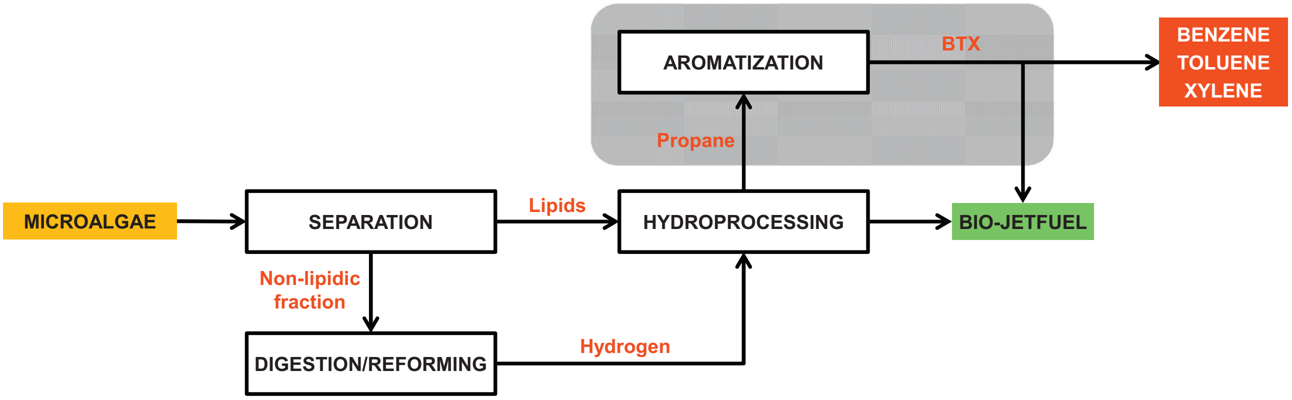

Fig. 1. Blocks diagram of a possible third generation zero-waste biorefinery.

According to Blakey and co-workers, one of the biggest concerns of alternative fuels has come from their low aromatic content. Concern has been raised that the ageing seals in the aircraft and engine would leak if the aromatic content is too low, as the seals would shrink. For this reason the aromatic content of synthetic fuel blends is currently fixed at a minimum of 8% (Blakey et al., 2011). On the other hand, Hui and co-workers studied the ignition and combustion of alternative jet fuels and they found that cetane numbers (CN) are higher than that of Jet-A. This is because Jet-A contains about 20% aromatics while HRJ consists mostly of iso-paraffin and cyclo-paraffin, which are less reactive compared to n-paraffins (Hui et al., 2012).

A strategy to produce HRJ fuel that satisfies this requirement is to blend it with aromatics produced from bio-based propane aromatization. The resulting integrated third generation biorefinery is illustrated in Fig. 1. This concept consists in a main hydroprocessing step of the algal oil, derived from the separation between the lipid and non-lipid fractions of the harvested microalgae. During this catalytic conversion, HRJ fuels are produced along with propane. This co-product is then aromatized over H-ZSM-5 catalyst to produce aromatics for blending and for sale on the petrochemical market. Unfortunately the selectivity towards high-value aromatics is reduced by the significant co-production of fuel gas (methane and ethane), which has a lower economic value. In general, zeolites with MFI pore structure are used, due to their high resistance to deactivation. Additionally, metal components, such as gallium, could be added to enhance the dehydrogenation function.

Nguyen and co-workers performed experimental and modelling studies of propane and n-butane aromatization over H-ZSM-5 zeolite at 500 °C in a wide range of conversions (Nguyen et al., 2006). Analysis of the experimental and kinetic modelling data has confirmed that propane and n-butane transformation over H-ZSM-5 occurs via both protolytic cracking of C—C and C—H bonds in paraffin molecules and hydrogen transfer between the propane and product olefins adsorbed on acid sites. Light olefins formed in the initial reaction steps give rise to fast oligomerization/cracking steps that control olefin distribution, as demonstrated in both the mechanistic studies of ethene and propene aromatization (Lukyanov et al., 1994) and propane aromatization (Lukyanov et al., 1994). Reaction kinetic studies of propane catalytic conversion to aromatics were also conducted by Bhan and co-workers on the same catalyst at atmospheric pressure and temperatures in the range of 520–550 °C, and different space times (Bhan et al., 2005). The same authors proposed additional investigations on the role of gallium modified zeolites (Bhan and Nicholas Delgass, 2008). The rates of production of several species are reported in both papers. They developed a kinetic model considering surface species as neutral alkoxides, reactions of these alkoxide species by carbenium ion-like transition states, and alkane activation by carbonium ion-like transition states.

Going further on, beyond the kinetic modelling and towards the plant scale, it should be noted that a global chemical process (e.g., propane aromatization process) consists of complex systems occurring at different levels, each with its own unique multi-scale structure (Li et al., 2005). The lack of commercial software able to integrate all these multidisciplinary features (Charpentier, 2009) drives the research towards the integration of different tools targeting different scales. Process System Engineering (PSE) provides numerical tools and platforms devoted to the investigation of the so-called Chemical Supply-Chain (Grossmann and Westerberg, 2000), which spans from the science-oriented study at the molecular level up to the system-oriented study of process networks and beyond.

This work proposes a new kinetic mechanism (micro and reactor scales) of propane aromatization, which is embedded in a multi-scale process simulation (process scale). The process simulation is performed with the PRO/II process modelling environment (PME), which has been extensively adopted both in the industrial and in the academic practice to model process plants that do not yet exist and to evaluate their economic viability (Lam et al., 2011). The necessity to include a custom process modelling component (PMC) derives from the choice of describing the catalytic reactor with a detailed surface kinetic mechanism. In the literature (Morales-Rodríguez and Gani, 2007) many efforts have been devoted to the definition of an efficient computer-aided framework to integrate PMCs in PMEs. For instance, the CAPE-OPEN standard has been widely adopted and integrated within PMEs. Applications of CAPE-OPEN standard in the field of PSE include, for instance, the modelling of thermodynamic properties and the modelling of new unit operations (Morales-Rodríguez et al., 2008). In both cases, the bridging between PMC and PME is obtained by a proper Middleware (e.g., CORBA, COM, .NET Framework).

The novelty of this work relies on the use of a different standard and Middleware. Particularly, Microsoft Excel is adopted to manage all communications between the PRO/II PME and the PMC (catalytic reactor unit), as outlined in Fig. 2. The advantage of this approach derives from its easiness and usability. In fact, home-made codes developed by engineers during R&D activities (e.g., regression of kinetic and thermodynamic models) could by directly embed within process simulators without the need for further modifications. Moreover, the use of the excel unit operation module allows directly post-processing and reporting simulation results in tables and graphs.

Section 2 addresses the reactor and kinetic modelling of propane aromatization on H-ZSM-5 catalysts; Section 3 shows results of the process simulation of the Cyclar process, performed