# Multi-Scale Simulation of Propane Valorization to BTX as a Co-Product from Algal Oil Hydroprocessing

Michele Corbetta[a], Flavio Manenti*[a], Lamia Zuniga Linan[b], Nádson M.N. Lima[b], Eliseo Ranzi[a], Sauro Pierucci[a]

[a]Politecnico di Milano, Dip. CMIC "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milano, Italy
[b]University of Campinas, Dep. of Process and Product Development, University City,13083-852,Campinas-SP,Brazil
flavio.manenti@polimi.it

Microalgae are a very promising and appealing feedstock for biofuels production. In fact, it is reported that some algal strains have very high oil content, even exceeding the 50 % of the dry weight. After growing and harvesting, algae require to be dewatered and the lipid fraction has to be separated. The obtained algal oil can be converted into alkyl esters by means of transesterification with an alcohol to produce biodiesel or may be treated with hydrogenation/cracking processes for the production of hydrocarbons, whose chemical structure is close to that of diesel fuels. Second generation processes for the production of drop-in biofuels from vegetable oils are based on hydrogenation reactions, which lead to the production of green diesel, and selective cracking reactions that maximize the production of bio-jet fuels $C_{10}$-$C_{15}$ fractions. These catalytic processes involve the cracking of triglycerides, saturation of double bonds, heteroatoms rejection (especially deoxygenation) and isomerization. Moreover, while glycerol is the low added value co-product for oils transesterification, propane represents more than 30 % of the final product in the hydrotreatment of the lipid fraction. Propane can be upgraded by selective conversion to aromatics, as additives for jet-fuels and versatile feedstocks for the chemical industry. The low selectivity to aromatics is the drawback of this process, resulting in a large production of cracking gases. In general, zeolites with MFI pore structure are used due to their high resistance to deactivation with metal components, such as gallium, added to enhance the dehydrogenation function. Kinetic studies of propane aromatization over H-ZSM-5 at 500 °C in a wide range of conversions are reported in the literature (Nguyen et al., 2006). Based on these and similar results (Bhan et al., 2005), a general kinetic model for propane aromatization has been developed. In this work the revised kinetic model is presented and embedded in a multi-scale simulation of a propane aromatization process, performed with the commercial code Invensys PRO/II (Kansha et al., 2009). Several technologies have been designed to directly convert LPG into aromatics (BTX). In this study the Cyclar process (Giannetto et al., 1994) developed by UOP and BP was selected.

## 1. Introduction

Third generation biomass conversion processes adopt microalgae as a raw material for the production of biofuels and bio-based chemicals. Two main technologies have been proposed for the conversion of the extracted lipidic fraction: methanol transesterification and hydroprocessing. While the first technology produces biodiesel (Bianchi et al., 2009), which is basically composed by a mixture of fatty acid methyl esters (FAMEs), the latter converts crude bio-oil into drop-in fuels, whose chemical composition resembles the petro-derived fuels. The conversion is obtained using methanol for the transesterification reaction and hydrogen for the hydroprocessing. Having as a target the zero-waste biorefinery, hydrogen could be produced from the non-lipidic fraction of microalgae through anaerobic digestion and/or reforming, as outlined in the conceptual scheme of Figure 1. Both technologies determine the production of low-value co-products, derived from the cleavage of triglycerides' backbone, which are glycerol and propane respectively. The current research activities are focused on processes able to enhance and valorize these co-products.
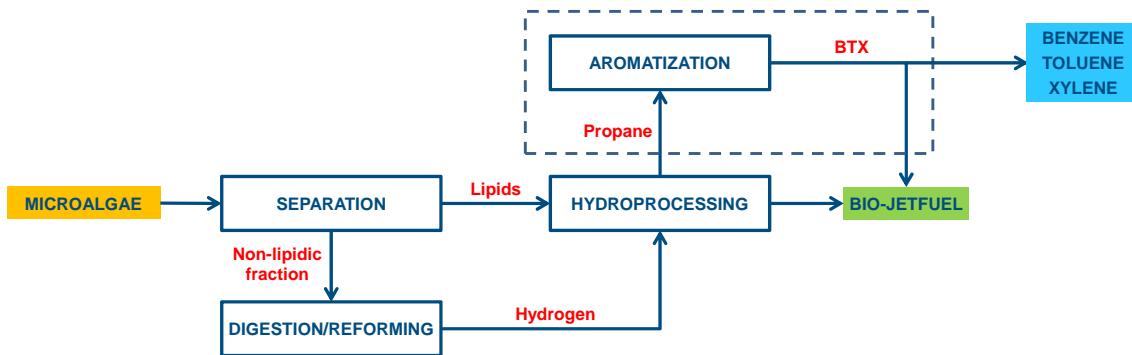
*Figure 1: Blocks diagram of a possible third generation zero-waste biorefinery.*

For instance, glycerol could be reformed in aqueous phase to produce hydrogen, a milestone component for the upgrading of bio-derived intermediates with an high oxygen content. Differently, propane could be converted to high value bulk chemicals such as BTX aromatics (as additives and intermediate chemicals). The chemical process relies on the catalytic acid function of mesopourous H-ZSM-5 zeolite, which is able to dehydro-cyclo-oligomerize light paraffins to aromatics through dehydrogenation, Commercial catalysts have a low selectivity and a large amount of fuel gas (especially methane and ethane) is produced along with aromatic products. For this reason it is of utmost importance to unveil the elementary surface chemistry involved, in order to guide the optimization of the catalyst design. Moreover, process simulation tools are necessary for the assessment of the economic viability and sustainability of the aromatization process. First, a kinetic model of the surface chemistry has been tuned and validated against experimental data. In the second part of the work, a process simulation of the BP/UOP Cyclar aromatization process has been performed with the commercial code PRO/II.

## 2. Kinetic modelling

Starting from the work of Nguyen and co-workers (2006), the kinetics of propane aromatization has been developed considering three different chemical classes (plus hydrogen), paraffins, olefins and aromatics, which are constituted by lumps of isomers with the same carbon number, in the range 1 to 8. Light paraffins (i.e. propane) dehydrocycloligomerization over H-ZSM-5 occurs via two routes: (i) protolytic cracking (PC) of C–C and C–H bonds in paraffins and (ii) hydrogen transfer (HT) between the feed propane and product olefins adsorbed on acid sites. Light olefins formed in the initial reaction steps give rise to fast alkene oligomerization/β-scission (cracking) reactions that control olefin distribution during propane aromatization. Finally, larger olefins are dehydrogenated and cyclize to aromatics through fast intermediates (dyenes, alkyl-cycloesenes and alkyl-cycloexadyenes), which are found experimentally just in traces (Figure 2).
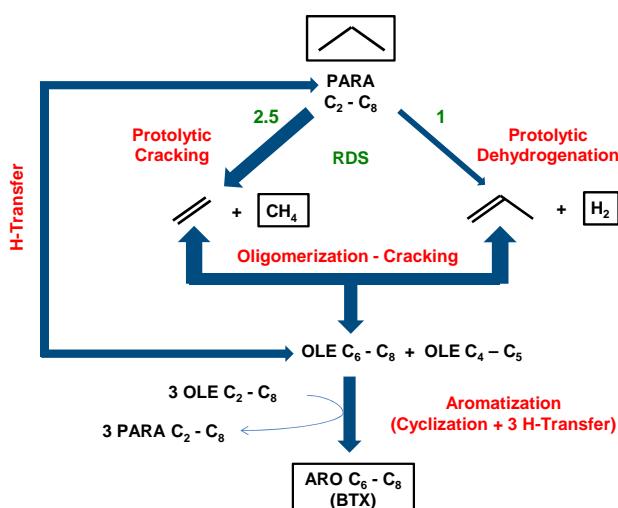


*Figure 2: Kinetic mechanism of propane aromatization*

Kinetics is the core of the reactor simulation. In our case reaction rates have been calculated according to an Ely-Rideal surface kinetic mechanism. In this way, the saturation of surface active sites by adsorbed aromatics and olefins is accounted for. This mechanism applies to the reaction between a gaseous species and an adsorbed one, which are A* and B in the example of Equation(1).

$$r = k_{kin}P_{A*}P_B = k_{kin}K_{ads}P_AP_B\theta_{free}\Omega = \frac{k' P_AP_B}{\left(1 + K_{ads,A}P_A + K_{ads,B}P_B\right)} \tag{1}$$

Where the partial pressure of an adsorbed species (i.e. A*) is calculated as the product between the partial pressure of the corresponding species in the gas phase, the adsorption constant ($K_{ads}$), the active site load ($\Omega$) and the free surface coverage ($\theta_{free}$), while $k_{kin}$ represents the kinetic constant. The effect of different models for the evaluation of $\theta_{free}$ will be discussed in Paragraph 2.2. The reactor is simulated with a pseudo-homogeneous isothermal PFR model, using the material balances reported below in Equation(2).

$$\frac{d\omega_i}{d\tau} = r_iMW_i \tag{2}$$

Where $\tau$ represents the ratio between the catalyst mass and the feed mass flowrate (i.e. the reciprocal of the WHSV), $\omega_i$ and $MW_i$ represent the mass fraction and the molecular weight of the i-th component.

## 2.1 Kinetic parameters

The kinetic constants have been estimated by non-linear regression (Buzzi-Ferraris and Manenti, 2009) using the guidelines provided in both the works of (Nguyen et al., 2006) and (Bhan et al., 2005), along with the available experimental data (Nguyen et al., 2006) of lab-scale H-ZSM-5 catalyst reactivity at 500 °C for different WHSV (Weight Hourly Space Velocity). Reactions are divided in 6 classes and the full set of stoichiometries is generated for each chemical lump involved. For instance, if we consider the protolytic dehydrogenation, the reaction determines the conversion of a paraffin to the corresponding olefin plus hydrogen. The reaction is then considered to all paraffins from propane up to the eight carbon paraffin with the same activation energy for each reaction class, as reported below.

*Table 1: Generated stoichiometries for the protolytic dehydrogenation*

| Protolytic dehydrogenation reactions |
| --- |
| n-$C_2$ > $C_2H_4$ + $H_2$ |
| n-$C_3$ > $C_3H_6$ + $H_2$ |
| n-$C_4$ > $C_4H_8$ + $H_2$ |
| n-$C_5$ > $C_5H_{10}$ + $H_2$ |
| n-$C_6$ > $C_6H_{12}$ + $H_2$ |
| n-$C_7$ > $C_7H_{14}$ + $H_2$ |
| n-$C_8$ > $C_8H_{16}$ + $H_2$ |

In Table 2 the range of the pre-exponential factors ($k_0$), the temperature exponents (n) and the activation energies ($E_a$) for each reaction class are provided, while Table 3 reports the two adsorption equilibrium constants for olefins and paraffins (Nguyen et al., 2006). Pre-exponential factors have units of measure consistent with partial pressures expressed in Pascal ([mol/g/h/Pa] or [mol/g/h/Pa$^2$]).

*Table 2: Kinetic parameters ($k_{kin} = k_0exp(-E_a/(RT))$)*

| Reaction class | $k_0$ | $E_a$ [kcal/mol] |
| --- | --- | --- |
| Protolytic dehydrogenation | 21 – 94 | 34 |
| Protolytic cracking | 72 – 187 | 34 |
| H-transfer | $2.9 \cdot 10^{-7}$ | 20.5 |
| Oligomerization | 0.002 – 0.4 | 30 |
| β-scission | 1 - 240 | 30 |
| Aromatization | $8.8 \cdot 10^{-9} – 0.0012$ | 7.2 |

*Table 3: Adsorption constants for the chemical classes*

| Lump | $K_{ads}$ [Pa$^{-1}$] |
| --- | --- |
| Olefins | $1.53 \cdot 10^{-7}$ |
| Aromatics | $7.81 \cdot 10^{-7}$ |

## 2.2 Results and comparisons

In the following section, some comparisons of the kinetic model simulations are provided with the experimental data (Nguyen et al., 2006). Figure 3 shows the evolution of the weight fractions of the main chemical species, propane, aromatics, $C_1$-$C_4$ paraffins, $C_2$-$C_4$ olefins and $C_{5+}$ lumps for different catalyst loads (i.e. different WHSV).
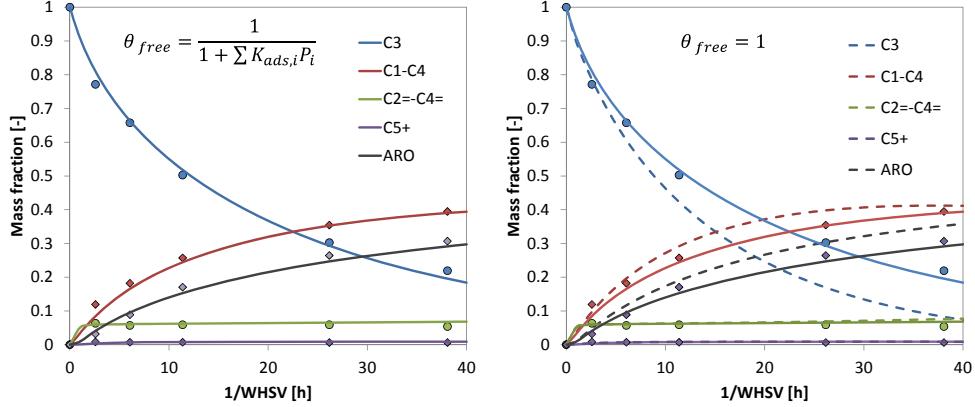


*Figure 3: Comparisons of model simulations and experimental data (Nguyen et al., 2006).*

Considering the highest catalyst load, propane is converted by 80 wt % mainly to light paraffins (≈ 40 wt %) and aromatics (≈ 40 wt %), thus the selectivity is close to 50:50 % for light paraffins and aromatics. Moreover, the effect of saturation is highlighted in Figure 3 by comparing full model results with Langmuir adsorption isotherm (solid line) with those obtained neglecting the evolution of the surface coverage (dashed line). It is possible to notice that it is necessary to account for the saturation effect in order to have a good reproduction of the reactivity of the system. Furthermore, a sensitivity analysis has been performed in order to figure out the role of the different reaction classes. Results are summarized in Figure 4.
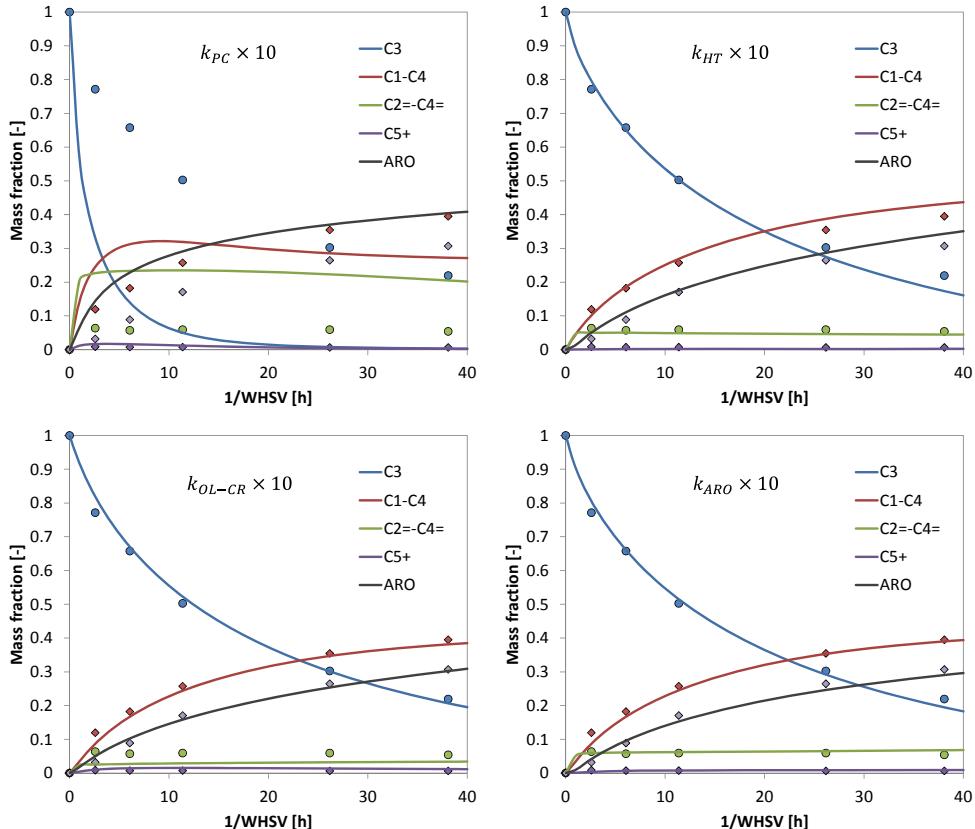


*Figure 4: Sensitivity analysis on reaction class kinetic constants*

The sensitivity analysis has been carried on by multiplying by ten all the reaction rates belonging to the same class. This analysis shows that the protolytic cracking/dehydrogenation is the limiting step, whose reaction rate is the smallest one (about 1000 times smaller than the other reactions). For this reason by multiplying kinetic constants of this step by ten, we obtain the larger effect. Increasing H-transfer rates results in a higher conversion of propane to light paraffins. On the other hand, oligomerization and cracking reaction classes don't affect the conversion of propane but slightly change the product distribution, mainly decreasing the amount of light olefins ($C_{2=}$-$C_{4=}$). Finally, the sensitivity of product distribution on aromatization rates appears to be negligible.

## 3. Process simulation

Once the kinetics has been validated against experimental data, they have been corroborated with a process simulation. The BP/UOP Cyclar aromatization process has been selected and simulated by means of the commercial code PRO/II.

The Cyclar process is composed by a catalytic section and a downstream section. The propane feed enters the catalytic reactor after a mixing step with the unconverted and recycled propane. Industrially, the reactor is a multiple inter-heated adiabatic annular moving-bed catalytic reactor. This unit has been simulated with a custom model, exploiting the Excel Unit Operation Module. In this way, the process simulator calls an excel file with a VB macro that runs a reactor model routine with the detailed kinetic model previously reported. The reactor effluent enters a FEHE and it is compressed and sent to a separator.

In the downstream section, the gas phase is further compressed and fed to a de-ethanizer, where the cut between ethane and propane is realized. Propane and heavies are recycled, while in the partial condenser a liquid stream rich in ethane (with methane) and a gas stream rich in methane (with hydrogen) are withdrawn. The liquid stream effluent from the flash is pumped to a stabilizer, where light hydrocarbons are stripped from the top and recycled to the catalytic section. From the bottom of the stabilizer, a liquid stream mianly composed of aromatics is fed to the last two purification columns. The first tower separates benzene from the top, while the last one separates toluene and xylene.

The material balances and thus the global performances of the plant are reported in Table 4, while in Table 5 and Table 6 reactor and distillation columns specifications are summarized respectively.
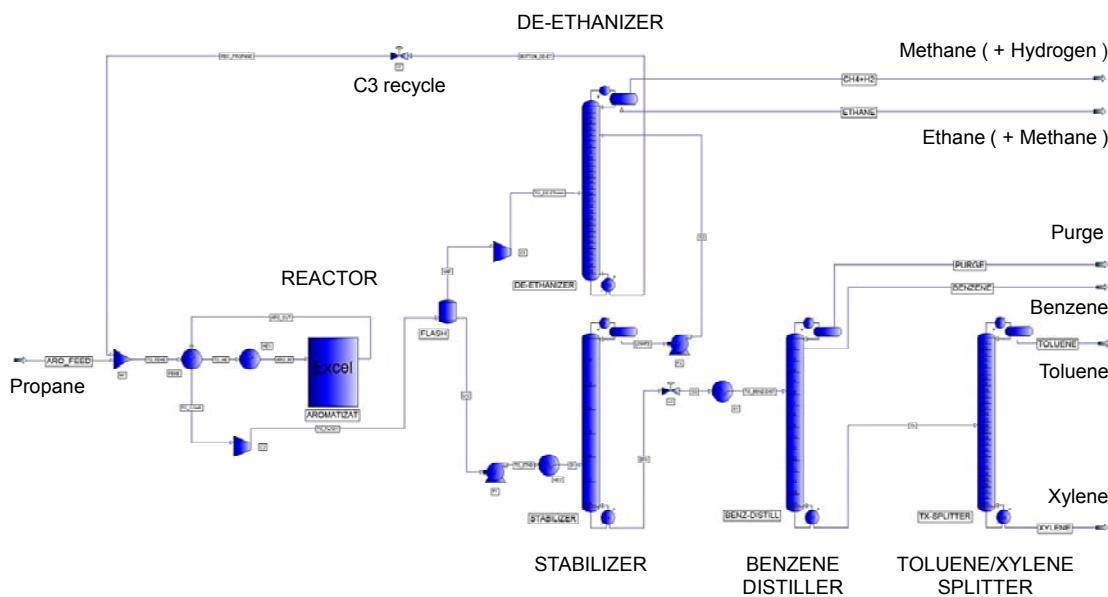


*Figure 5: Flowsheet of the Cyclar process simulated with the commercial software PRO/II.*

*Table 4: Global material balances*

| Stream | Mass flowrate [ton/h] | Molar flowrate [kmol/h] | Mass fraction of the key component [-] |
|---|---|---|---|
| Propane (feed) | 4.410 | 100 | 1.00 |
| Fuel gas $C_2H_6$ - $CH_4$ (70-30 % mol) | 0.790 | 29.7 | 0.78 |
| $CH_4$ - $H_2$ - $C_2H_6$ (60-30-10 % mol) | 1.820 | 134 | 0.69 |
| Benzene | 0.484 | 6.20 | 0.97 |
| Toluene | 0.910 | 9.91 | 0.96 |
| Xylene | 0.396 | 3.74 | 0.99 |
| Purge (propane - benzene) | 0.010 | 0.21 | 0.40 |

*Table 5: Reactor specifications*

| | | Specification |
|---|---|---|
| Reactor temperature | [°C] | 500 |
| Reactor pressure | [bar] | 1.2 |
| Catalyst load | [ton] | 325 |
| Propane conversion (mass) | [-] | 0.900 |
| BTX yield (mass) | [-] | 0.373 |

*Table 6: Distillation columns specifications*

| | | DE-ETHANIZER | STABILIZER | BENZ-DISTILL | TX-SPLITTER |
|---|---|---|---|---|---|
| Number of trays | [-] | 30 | 9 | 17 | 30 |
| Condenser pressure | [bar] | 20 | 10 | 1.2 | 1.2 |
| Condenser temperature | [°C] | -74 | -78 | 49 | 115 |
| Condenser duty | [kW] | -491 | -23 | -555 | -214 |
| Reboiler duty | [kW] | 57 | 134 | 572 | 215 |
| Reflux ratio | [-] | 0.6 | 1 | total | 1.32 |

## 4. Conclusions

A detailed model for the surface kinetic mechanism of propane aromatization was proposed and validated against experimental data. Basing on kinetics, a BP/UOP Cylar process simulation has been performed with the PRO/II commercial simulator. The chemistry of the process under study has been corroborated with the simulation by Excel User-Added Model. The predictivity of the multi-scale model was strengthened in a wider range of operating conditions. The results of this work open up the possibility of using the same process optimization for future works dealing with the integration of the propane aromatization with the hydroprocessing of algal oil (amount of aromatics blended in algal-oil derived jet-fuels) and could provide reliable information for an economic evaluation.

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