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Multi-Scale Simulation of Propane Aromatization as a Recovery Process in the Microalgae-to-Oil Conversion

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In this study a multi-scale simulation of the propane aromatization process is presented. The recent interest in this technology derives from the development of new conversion routes of third generation biomass. Advanced processes for the production of drop-in biofuels from vegetable (e.g. algal) oils are based on hydrogenation reactions, which lead to the production of green diesel, and selective cracking reactions that maximise 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 (Bianchi et al., 2009), propane represents more than 30 % of the final product in the hydrotreatment of the lipid fraction. Propane can be upgraded by catalytically convert it to aromatics, which are additives for jet-fuels and bulk feedstock for the chemical industry. The low selectivity towards aromatics strongly reduces the efficiency of the overall process, caused by a large production of cracking gases. In general, zeolites with MFI pore structure are used due to their high resistance to deactivation (Pirola et al., 2010) with metal components, such as gallium, added to enhance the dehydrogenation function. Kinetic studies of propane aromatization over H-ZSM-5 at 500 °C and atmospheric pressure 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 the multi-scale simulation of a propane aromatization process, performed with the commercial code Invensys PRO/II. 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

The high oil content of some microalgae strains, even exceeding the 50% dry weight, makes them suitable as a feedstock for the production of liquid hydrocarbons for fuel and chemical applications. This oil fraction could be recovered from microalgae after harvesting and upstream processing. During this phase cells are separated from water and they are disrupted in order to release the lipid content. The recovered lipid fraction is mostly constituted by triglycerides with too high oxygen contents. To enhance the quality of the bio-oil an upgrading step is mandatory. Commonly triglycerides are converted to biodiesel by means of transesterification, while a smarter route seems to be the hydroprocessing of the bio-oil to produce drop-in fuels in the range of jet-fuels (HRJ-fuels) and green diesel. These kind of catalytic processes involve the cracking of triglycerides, saturation of double bonds, deoxygenation and isomerization. As a result, large amounts of propane are co-produced from the cleavage of the oxygenated triglyceride head. Propane represents more than the 30 % of the final product, and it can be upgraded by a selective catalytic conversion process to aromatics, as additives for jet-fuels and flexible feedstocks for the chemical industry. The aromatization process converts light paraffins to BTX and hydrogen along with a significant amount of light fuel gases, mainly composed by methane and ethane, which could not be further converted, reducing the selectivity of the process. In general MFI zeolites are adopted due to their high resistance to

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deactivation by coke deposition and pore blocking. Metal components, such as gallium, could be added as promoters to enhance the catalytic 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), and they constitute a useful starting point for the definition of a general kinetic scheme. Following these indications, a kinetic model for propane aromatization has been developed and discussed. According to the literature, the first step is propane activation on the catalyst surface through protolytic cracking and hydrogen transfer with adsorbed olefins. Light olefins formed in the initial reaction step give rise to fast alkene oligomerisation and cracking reactions that control olefin distribution during the process. Bigger olefins are then converted to aromatics through cyclization and dehydrogenation.

In this work a multi-scale simulation of the aromatization process (Figure 1) is performed in order to assess the economic viability of the technology. For this purpose, the kinetic model is embedded in a process simulation, performed with the commercial code Invensys PRO/II. Several technologies have been designed to convert LPG into BTX; in this study the Cyclar process (Giannetto et al., 1994) developed by UOP and BP was selected.

2. Kinetic modelling

A kinetic model of propane aromatization on H-ZSM-5 catalyst has been developed based on the available literature (Nguyen et al., 2006). The present model considers 19 (pseudo)components divided in three different chemical groups (plus hydrogen), which are paraffins, olefins and aromatics. Each group is constituted by lumps of isomers with the same carbon number in the range of 1 to 8. The full set of 83 chemical reactions belongs to 6 different classes: C-H and C-C protolytic cracking, H-transfer, oligomerization, cracking and aromatization. Light paraffins dehydrocycloligomseriation occurs via two routes: (i) paraffins protolytic cracking and (ii) hydrogen transfer between propane and produced olefins adsorbed on acid sites. Light olefins produced in the initial reaction steps give rise to fast alkene oligomerisation/cracking reactions that control olefin distribution. Finally, larger olefins are dehydrogenated and cyclize to aromatics through fast intermediates. In our model, reaction rates have been calculated according to an Eley-Rideal surface kinetic mechanism, to account for the saturation of surface active sites by adsorbed aromatics and olefins. Reaction rates are embedded in a reactor simulation adopting an isothermal pseudo-homogeneous PFR model (Equation 1), where ω stands for the mass fraction, tau is the reciprocal of the Weight-Hourly-Space-Velocity (WHSV), MW is the molecular weight. Kinetic constants k_{KIN} are expressed with a modified Arrhenius expression (Equation 1).

$$\frac{d\omega_i}{d\tau} = r_i MW_i = k_{KIN} \frac{\prod_{i=1}^{Nreact} C_i}{1+\prod_{j=1}^{Nads} K_{ADS,i} C_j} MW_i = A \cdot T^n \exp\left(-\frac{E}{RT}\right) \frac{\prod_{i=1}^{Nreact} C_i}{1+\prod_{j=1}^{Nads} K_{ADS,i} C_j} MW_i \tag{1}$$

2.1 Non-linear regression

The non-linear regression of the kinetic parameters was performed by means of the set of robust optimizers belonging to the BzzMath library (Buzzi-Ferraris and Manenti, 2012). Representative reaction kinetics are provided in Table 1, while comparisons with experimental data (Nguyen et al., 2006) are provided in Figure 2. Such optimizers are based on the object-oriented programming and parallel computing in order to reduce the computational time. They have implemented numerical methods able to simultaneously handle the narrow-valley problem, which typically arise in the estimation of kinetic parameters (Buzzi-Ferraris and Manenti, 2009) and the possible presence of bad-quality measures with the identification of outliers.

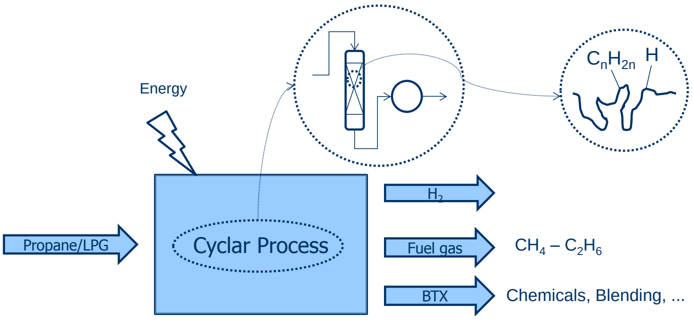


Figure 1: Multi-scale representation of the aromatization process

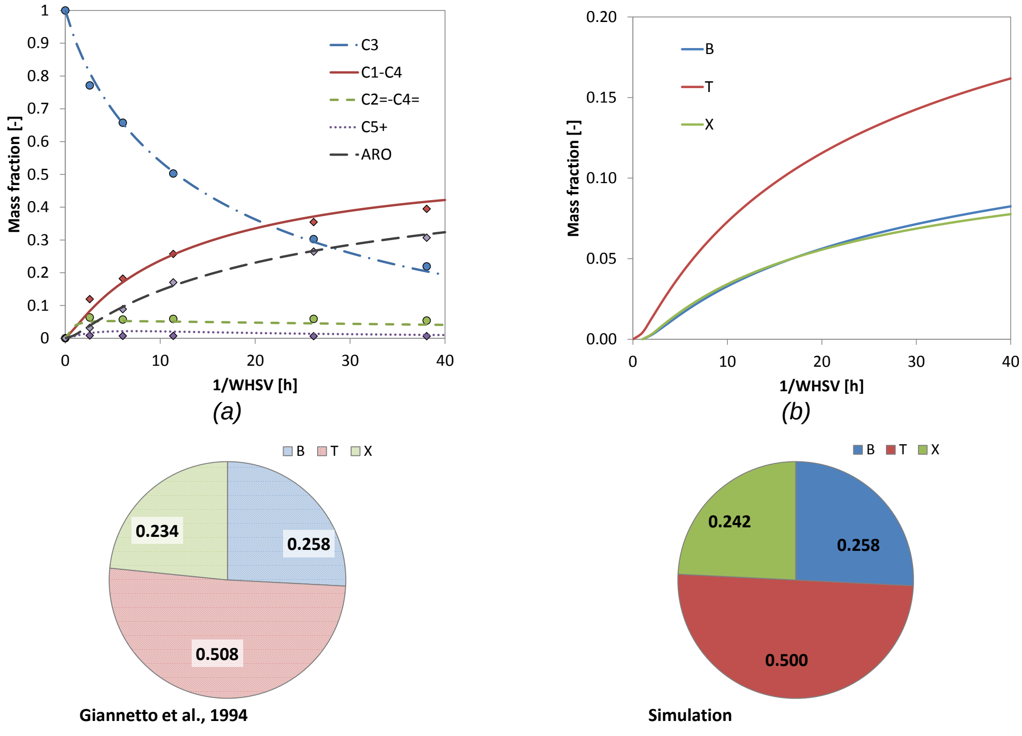
Table 1: Representative reaction kinetics of propane aromatization over H-ZSM-5 catalysts

Reaction	A	n	E [cal/mol]
Protolytic Cracking C-H			
n-C_2 > OLE2 + H_2	43,538	1	34,000
n-C_3 > OLE3 + H_2	43,538	1	34,000
n-C_8 > OLE8 + H_2	191,568	1	34,000
Protolytic Cracking C-C			
n-C_3 > OLE2 + CH_4	146,929	1	34,000
n-C_8 > OLE2 + n-C_6	382,016	1	34,000
n-C_8 > OLE3 + n-C_5	382,016	1	34,000
n-C_8 > OLE4 + n-C_4	382,016	1	34,000
n-C_8 > OLE5 + n-C_3	382,016	1	34,000
n-C_8 > OLE6 + n-C_2	382,016	1	34,000
n-C_8 > OLE7 + CH_4	382,016	1	34000
H-Transfer			
n-C_3 + OLE2 > OLE3 + n-C_2	4.91191	2	20,545
n-C_3 + OLE4 > OLE3 + n-C_4	4.91191	2	20,545
n-C_3 + OLE5 > OLE3 + n-C_5	4.91191	2	20,545
n-C_3 + OLE6 > OLE3 + n-C_6	4.91191	2	20,545
n-C_3 + OLE7 > OLE3 + n-C_7	4.91191	2	20,545
n-C_3 + OLE8 > OLE3 + n-C_8	4.91191	2	20,545
Oligomerization			
OLE2 + OLE2 > OLE4	28,859	2	2,9861
OLE2 + OLE3 > OLE5	490,608	2	2,9861
OLE2 + OLE4 > OLE6	952,358	2	2,9861
OLE2 + OLE5 > OLE7	952,358	2	2,9861
OLE2 + OLE6 > OLE8	952,358	2	2,9861
OLE3 + OLE3 > OLE6	1,038,938	2	29861
OLE3 + OLE4 > OLE7	4,588,649	2	2,9861
OLE3 + OLE5 > OLE8	6,666,496	2	2,9861
Cracking (beta-scission)			
OLE4 > OLE2 + OLE2	2,121	1	2,9861
OLE5 > OLE2 + OLE3	36,057	1	2,9861
OLE6 > OLE2 + OLE4	69,993	1	2,9861
OLE7 > OLE2 + OLE5	69,993	1	2,9861
OLE8 > OLE2 + OLE6	69,993	1	2,9861
OLE6 > OLE3 + OLE3	76,356	1	2,9861
OLE7 > OLE3 + OLE4	337,239	1	2,9861
OLE8 > OLE3 + OLE5	489,945	1	2,9861
Aromatization			
OLE6 + 3 OLE2 > BENZ + 3 n-C_2	0.165438	2	7,167
OLE7 + 3 OLE2 > TOLU + 3 n-C_2	186.1184	2	7,167
OLE8 + 3 OLE2 > XYL + 3 n-C_2	0.187998	2	7167
OLE6 + 3 OLE8 > BENZ + 3 n-C_8	6.617545	2	7,167
OLE7 + 3 OLE8 > TOLU + 3 n-C_8	7444.746	2	7,167
OLE8 + 3 OLE8 > XYL + 3 n-C_8	7.519941	2	7,167

2.2 Sensitivity analysis

A sensitivity analysis of kinetic constants on product distribution has been performed by multiplying by ten pre-exponential factors of a given reaction class. Results are summarized in Figure 3.

This analysis shows that the protolytic cracking/dehydrogenation is the rate determining step of the overall scheme. This is further confirmed by the fact that its kinetic constant is about 1,000 times smaller with respect to the other reaction classes. For this reason by multiplying kinetic constants of this step by ten, it results in the larger effect. Increasing H-transfer rates lead to a higher conversion of propane to light paraffins. On the other hand, oligomerisation and cracking reaction classes don't affect the conversion of propane but change the distribution between C_{5+} and $C_{2=}$-$C_{4=}$. Finally, the sensitivity of product distribution on aromatization rates appears to be negligible.



(a) (b)

(c) (d)

Figure 2: Comparisons of the kinetic model with experimental data (Nguyen et al., 2006). (a) Product yields: experimental data (symbols) and model predictions (lines). (b) Average aromatics mass distribution: literature data (c) and model prediction (d)

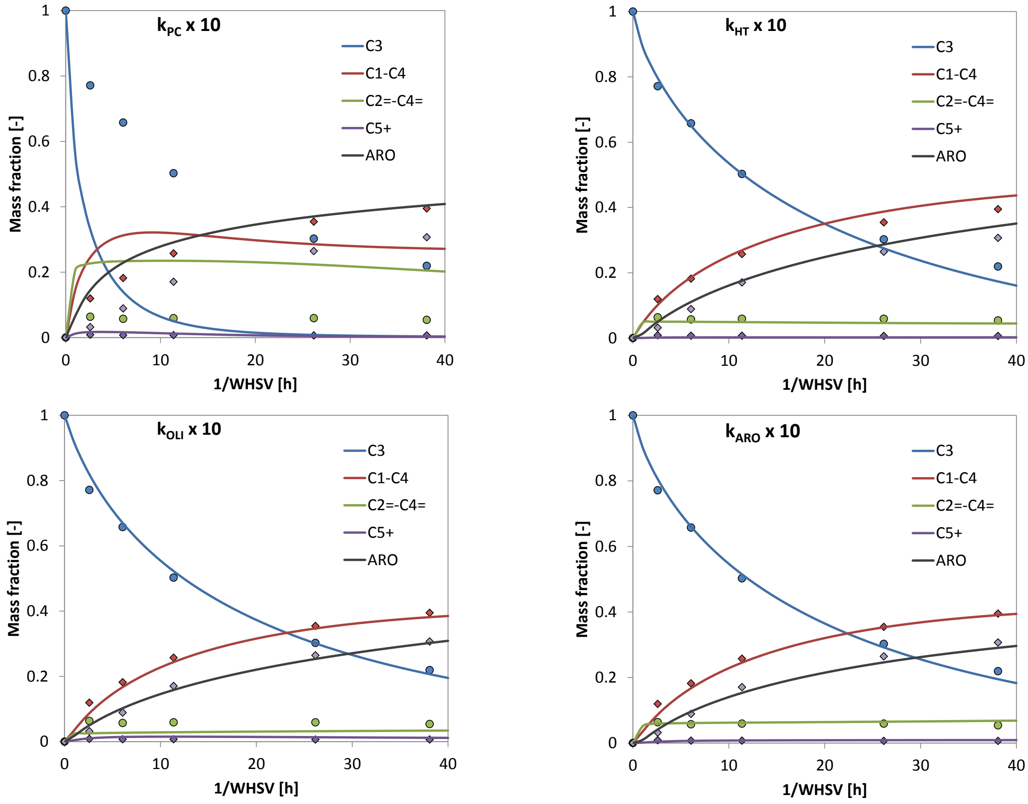


Figure 3: Sensitivity analysis of kinetic constants on product yields

3. Process simulation

Once the kinetics has been validated against experimental data, they have been embedded within a process simulation. The BP/UOP Cyclar aromatisation process has been selected and simulated by means of the commercial code PRO/II (Figure 4).

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 consists in 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 Visual Basic macro that runs a reactor model routine with the detailed kinetic model previously reported. The reactor effluent enters a Feed-Effluent-Heat-Exchanger (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-ethaniser, where the cut between ethane and propane is realized. Propane and heaviers 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 de-ethaniser. From the bottom of the stabiliser, a liquid stream mainly 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 2.

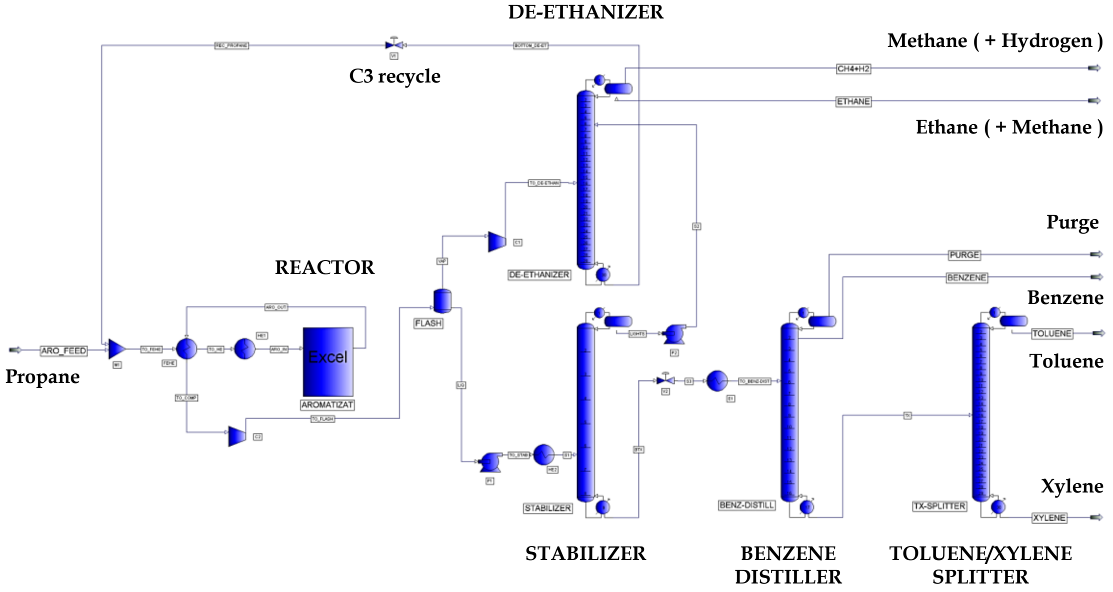


Figure 4: Cyclar process layout

Table 2: Global material balances

Stream	Mass flowrate [t/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	0.206	0.40

3.1 Economic considerations

In order to evaluate the economic sustainability of the process, costs of raw materials and prices of products have been collected in Table 3.

Table 3: Economic parameters

Chemical compound	Unit cost/price [€/kg]	Economic flux [€/h]	Reference
Propane	0.599	-2641.6	2013 PLATTS LPGASWIRE
Ethane	0.022	17.38	2013 PLATTS
Methane	0.058	101.3	2013 PLATTS
Hydrogen	1.45	105.56	(Doty, 2004)
Benzene	0.982	475.3	2013 PLATTS
Toluene	0.941	856.3	2013 PLATTS
Xylene	1.165	461.3	2013 PLATTS

In our calculations, we assumed to be able to separate hydrogen methane and ethane from the fuel gas stream. Now it is possible to evaluate the 2nd order Economic Potentials as follows:

$$EP_2 = \sum_{j=1}^{NP} €_{P,j} n_j - \sum_{i=1}^{NR} €_{R,i} n_i = -604€/h \qquad (1)$$

4. Conclusions

A detailed model for the surface kinetic mechanism of propane aromatization over H-ZSM-5 catalyst was proposed and validated against experimental data. Basing on kinetics, a BP/UOP Cyclar process simulation has been performed with the PRO/II commercial simulator. The chemistry of the process under study has been imbedded within the process simulator by the 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 for future works dealing with the integration of the propane aromatization with the hydro processing of algal oil and it could provide reliable information for an economic evaluation. The second order economic potential shows a strong penalty derived from the low selectivity towards aromatics. In fact, the production of large amounts of low-value fuel gas (i.e. methane and ethane) drastically reduces the profitability of the process. Accordingly, new insights in more selective catalysts appear to be the best research direction for the ongoing activity. This line of research appears to be promising, according to the development of catalysts with higher selectivities toward aromatics (up to 80 %) reported in the literature (Wang et al, 2002), which are active also in methane aromatization (Shu et al., 1999), thus reducing the amount of fuel gas. Moving from the kinetic modelling of the basic H-ZSM-5 catalyst, future works will deal with the analysis of new metal promoted zeolite catalysts.

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