Simulation and Optimization of a Multitubular Reactor Train for Acrylic Acid Production

David Lokhat*, Kiara Premlall

School of Engineering, University of KwaZulu-Nata, Durban, 4041, South Africa
lokhat@ukzn.ac.za

Acrylic acid is a major chemical intermediate used in the production of acrylate esters. The most popular route for the manufacture of ester grade acrylic acid is via propylene oxidation. In a typical process, chemical grade propylene is contacted with steam and air in a catalytic reactor train to produce the target compound with carbon dioxide and acetic acid as the major byproducts. Various catalytic systems exist, offering both high selectivity and conversion, and operation can be based on different reactor types and configurations. The highly exothermic nature of the reactions necessitates efficient removal of the reaction heat. In this work the rigorous simulation and optimization of a two-step multitubular oxidation reactor system for the production of acrylic acid was undertaken on the ASPEN Plus platform, with particular emphasis on minimizing energy requirements. In developing the model, several critical parameters were identified for proper representation of the reaction system in the sequential simulation platform. These included adjustments to the properties of molten salt thermal fluids for accurate determination of flow characteristics on the shell side, comprehensive and interactively coupled calculation of the overall heat transfer coefficient and the use of inert pre-heating and oxidation pre-heating zones at the front end on the propylene oxidation reactor tubes. The resultant model was successfully used to optimize for acrylic acid production with minimum energy input, demonstrating the applicability of digital twins for process analysis.

1. Introduction

Acrylic acid is an important industrial chemical used as a raw material in a wide variety of consumer end products. It is a colourless liquid with a distinctive and acrid smell. There are two grades of acrylic acid which are commercially available; technical (ester) grade and glacial grade. Ester grade acrylic acid is approximately 94% purity by mass and is converted to acrylate esters (Petrescu et al., 2016). The esters are converted to co-monomers which when polymerized are used to make surface coatings, adhesives, sealants, textiles and paint. Glacial acrylic acid is generally 99.5 – 99.7 % purity by mass and is polymerized to produce polyacrylic acid-based polymers (Petrescu et al., 2016). These polymers are used to make detergents, dispersants, super absorbent polymers (such as in diapers) and thickeners (Beerthuis et al., 2015).

Acrylic acid is produced on a commercial scale by the gas phase catalytic oxidation of propylene via acrolein. The reaction can be carried out in single or two-step process, however the latter is favoured due to higher reported yields (Rase, 2000). The two-step oxidation route uses a vapour phase heterogeneous catalysis system. In the first reaction stage, propylene is oxidized with air and steam to acrolein and subsequently fed to the second stage where the acrolein is oxidized to acrylic acid (Rase, 2000). The first stage catalyst is a mixed metal oxide catalyst composed of mainly of molybdenum and bismuth oxides. The second stage catalyst is also a complex mixed metal oxide catalyst composed primarily of molybdenum and vanadium (Nojiri et al., 1995).

Due to the highly exothermic reactions occurring in the reactors, the removal of the heat of reaction is required. To ensure this, the reactors are usually of the multitubular fixed bed type with a heat transfer medium (usually molten salt) circulating through the reactor shell (dos Santos et al., 2018). The large amount of heat generated through the reaction can be exploited for energy utilization on the plant. The design, optimization and analysis of such a unit is a complicated task, since there are a large number of optimization variables to be considered. Proper representation of the reactor train in a process simulator is the first step towards heat integration, development of energy management strategies and overall understanding that could lead to intensification of

the process (Tripodi et al., 2017). Process simulation studies carried out on this process and reported in the literature have considered either adiabatic or fluidized bed reactor types with no in depth analysis of the more popular multitubular reactor configuration (Suo et al., 2015). In this work, the rigorous design of a two-stage acrylic acid reactor train was undertaken and critical parameters identified for accurate representation of the unit in a process simulation platform. The study offers insight into the sensitivity of major performance criteria to the various operating parameters, many of which are unique to the multitbular reactor configuration.

2. Process simulation

2.1 Reactor configuration

Propylene and acrolein partial oxidation reactions are highly exothermic, with reaction kinetics that are sensitive to changes in temperature and therefore susceptible to thermal runaway and catalyst degradation. As such, effective heat removal is essential to maintain production rates and avoid irregular hot spots within the reactor. Presently, exothermic reactions for acrylic acid production occurs in multi-tubular reactors consisting of up to 30,000 tubes with small diameters to ensure that thermal radial gradients are reduced whilst increasing the available heat exchange area for optimal and rapid heat removal by a circulating heat transfer fluid on the shell side (Jiang, et al., 2015). This configuration was chosen for the simulation. The co-current flow arrangement was selected since the maximum heat driving force is available at the beginning of the reactor, where the concentration of reactants is maximum and so is the reaction rate. Therefore, the heat transferred is also highest (Borio, et al., 1989). Molten salt heat transfer fluids were chosen due to their practicality for high temperature applications.

2.2 Reaction Kinetics

Reaction kinetics for the partial oxidation of propylene over a bismuth molybdate catalyst were extracted from Redlingshofer et al. (2003). Acrolein oxidation to formaldehyde was considered negligible due to the low range of selectivities reported in the literature i.e. 0.73 – 0.78 % (Redlingshofer, et al., 2002). The redox reaction mechanism for acrolein formation exists in two counterparts i.e. reduction and oxidation reactions. Models such as the Mars-van-Krevelen and Langmuir-Hinshelwood rate expressions account for the crossover from oxidation to reduction reactions in a single expression however, the power law reduction reaction was favoured since the α-bismuth molybdate catalyst selected, which has a high selectivity to acrolein of 88 – 95 % operates optimally in a temperature range of 623 – 723 K (Redlingshofer, et al., 2003). Kinetics for the partial oxidation of acrolein to acrylic acid were taken from Estenfelder and Lintz (2002) for the range 533 – 573 K.

2.3 Simulation approach and optimization strategy

The reactor feed materials used in the simulation of the acrylic acid process was assumed to consist of a mixture of chemical grade propylene with a molar based purity of 94 % (containing equimolar impurities of ethane and propane, which are considered to be inerts in this system); low pressure steam at 3 - 5 bar and air at 298 K and 1 bar. Propylene is assumed to be routed from an existing network on site at a temperature of 303 K and 11 bar. The reactions take place in two reactors, designated R-101 and R-102, as shown in Figure 1.
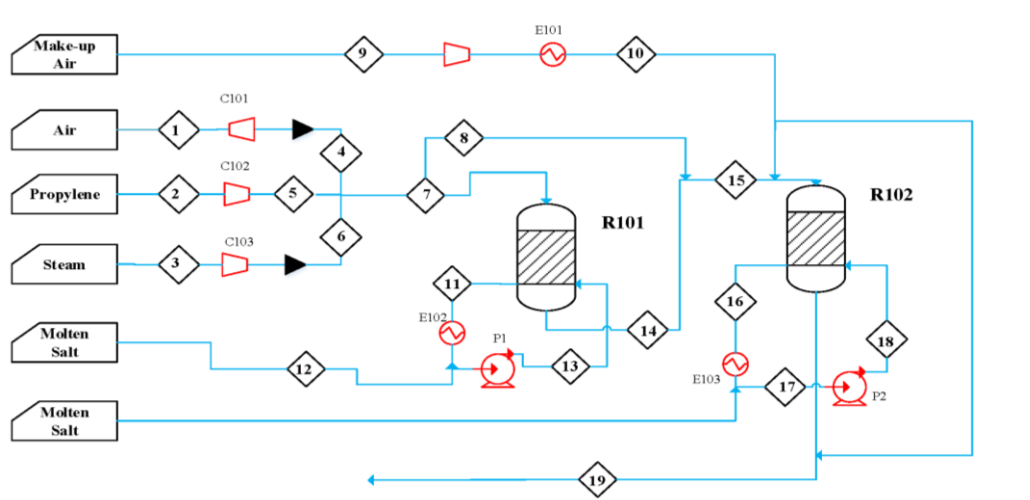

Figure 1: Process flow diagram for acrylic acid production

Literature reported a 2-5 bar operating pressure range for Reactor R-101 therefore a 5 bar pressure was selected. Reactor R-101 operates at a peak temperature found to be in the range of 633 - 703 K and a pressure of approximately 5 bar. Reactor R-102 is required to operate at a peak temperature in the range of 533 - 573 K and a pressure of approximately 4 bar.

The RPLUG model on Aspen Plus® assumes ideal plug flow characteristics for the reacting system therefore radial velocity gradients were considered negligible. Interphase heat and mass transfer resistances and axial dispersion were also neglected. Since both heat and mass transfer coefficients increase with increasing mass velocities, in most industrial reactors with large throughputs at high pressures, it is practical to avoid significant interphase gradients. Axial and radial dispersion was neglected since the tube length to particle diameter was large. The overall heat transfer coefficient (OHTC) in a multi-tubular reactor can have a direct influence on the size of the reactor unit. The overall heat transfer coefficient was initially estimated. A macro enabled Excel spreadsheet was coupled with the Aspen PLUS® simulation to read in the simulation outputs and export the pressure drop and OHTC values which were calculated using methods outlined in literature (Sinnot, 2005). This calculation was carried out iteratively until convergence. Preliminary base case reactor simulations showed large tube side pressure drops that were not conforming to the allowable 10 % for economical and practical industrial reactors. Spherical catalyst particles are commonly used for propylene partial oxidation in industry, the catalyst geometry was revised. The use of hollow cylinder catalyst pellets enhances conversion levels in reactors due to the better utilization of the catalytic material, with the most notable feature being the absence of the pellet core which lowers internal transport resistances and the reactor pressure drop (Asif, 2013). This catalyst geometry was selected for further simulation work.

Approximately the same optimisation methodology was applied to reactors R-101 and R-102. The purpose of the optimisation was to size the reactors such that the conversion of propylene and acrolein were ~95 % and ~100 %, whilst maximizing the overall selectivity to the target compounds and minimizing the flowrate of cooling fluid (molten salt) required. This would then translate into lower cooling costs and hence energy usage. The optimization considered the following variables:

- Reactor length
- Coolant fluid flowrate
- Coolant fluid inlet temperature
- Number of tubes

The diameter of the tubes was selected to be 1 inch based on design heuristics reported in the literature (Rase, 2000). The optimization was subject to the following constraints:

- Temperature within reactor R-101 between 633 and 703 K
- Temperature within reactor R-102 between 533 and 573 K
- Tube side pressure drop below 10% of total pressure
- Conversion of propylene in reactor R-101 above 95 %
- Conversion of acrolein in reactor R-102 practically 100 %. This is required since downstream separation processes require practically total conversion of acrolein.

Due to the heavily coupled nature of the parameters, the independent sensitivity of each variable was difficult to determine even when using combinations of Optimisation, Sensitivity and Design Spec/Vary models in Aspen Plus®. Consequently, algorithms were developed that utilised the aforementioned model analysis tools on Aspen Plus® together with manual (offline) iterations. The optimisation algorithms for R-101 and R-102 were similar, with differences due to the varying extents of the respective exothermic reactions. Temperature ranges and hotspot formation were more difficult to control in R-102 as compared to R-101 hence rigorous design changes to R-102 were made, to be discussed in the next section. A variety of adaptations from literature and patent literature regarding the control of exothermic reactions was reviewed such that different reactor geometry trials could be tested in ensuring the most optimum reactor design for R-102.

The optimisation procedure entailed manually adjusting the tube length to determine the most efficient length for the reactor. The reactor tube length affects the tube and shell pressure drops since the Ergun equation and general shell side pressure drop correlations are directly proportional to tube length. In addition, the tube length determines the overall dimensions of the reactor since the tube length is inversely proportional to the number of tubes. The tube length was therefore varied manually whilst Aspen Plus sensitivities were used to determine the minimum number of tubes required for the respective tube length as well as the optimum coolant inlet temperature and flow rate.

There exists a strong interaction between the shell and tubes due to the molten salt temperature profile which is dependent on both the exothermic reactions occurring within the tube and the differing interactions between the molten salt and each individual tube. Due to the highly exothermic nature of the partial oxidation reactions in R-101 and R-102 as well as the likelihood of hot spots, the aforementioned critical parameters were required to be paired in a particular manner to ensure convergence. Sensitivities were conducted on the heat transfer fluid flow rate and inlet temperature using a base case reactor to determine which variable controlled the

maximum and minimum temperatures within the reactor. For R-101, the heat transfer fluid flow rate affected the minimum temperature the most whilst the maximum temperature was affected by the heat transfer fluid inlet temperature the most. The same behaviour was observed for reactor R-102.

3. Optimization results

The optimized reactor unit R-101 contained 10,000 tubes with a length of 2.8 m housed in a cylindrical shell. The total flowrate of molten salt cooling fluid was 340 kg·s⁻¹ at an inlet temperature of 666 K. The total duty for the unit was approximately 30 kW. In the base case design, the outlet temperature of the cooling fluid was well above its inlet temperature. Following the optimisation procedure outlined in the previous section, an inert preheating zone was added to R-101 to utilise the heat carried by the molten salt circulating in R-101 to preheat the feed and regulate the increase in cooling fluid temperature. This concept was taken from the production of phthalic anhydride.

Initially, R-101 was divided into an inert preheating zone and an optimized reacting zone. The resultant molten salt temperature exiting the optimised reactor zone was at 689 K. In order to preheat R-101 feed from 363 K to the required temperature of 633 K for the propylene reduction reaction, an Aspen Plus® simulation was conducted to determine the inlet molten salt temperature needed as well as the length of the inert zone. The length of the preheating zone was restricted by the tube side pressure drop, since the inlet temperatures and pressures from the preheating zone had to be equal to the inlet temperatures and pressures into the reacting zone. Unfortunately, due to the low feed temperature, the maximum temperature of the feed in the preheating zone reached 623 K. Therefore, in order to further increase the feed to the required 633 K, the propylene oxidation reaction occurred in a 0.5 cm length in reactor R-101 forming a negligible amount of acrolein. The reacting zone was thereafter re-optimised however the geometry did not change due to the small quantity of acrolein formed in the preheating zone. Reactor R-101 is essentially 3 series reactors with an inert preheating zone, an oxidation preheating zone and a reacting zone. Optimisation was conducted for the reacting zone since this is the pivotal part of reactor R-101. The preheating zone was used as part of energy optimisation since the temperature of molten salt needed to heat the feed to 633 K was close to the exiting molten salt temperature. The resultant temperature and composition profiles in R-101 are presented in Figure 2. Using this strategy, the outlet temperature of the molten salt was brought to within 20 K of its inlet temperature and reduced the flowrate requirement by 15 %. These collectively resulted in an energy saving of approximately 5% based on pumping and utility cooling costs, taking into account the steam credit usually obtained from the spent cooling fluid in a waste heat boiler.
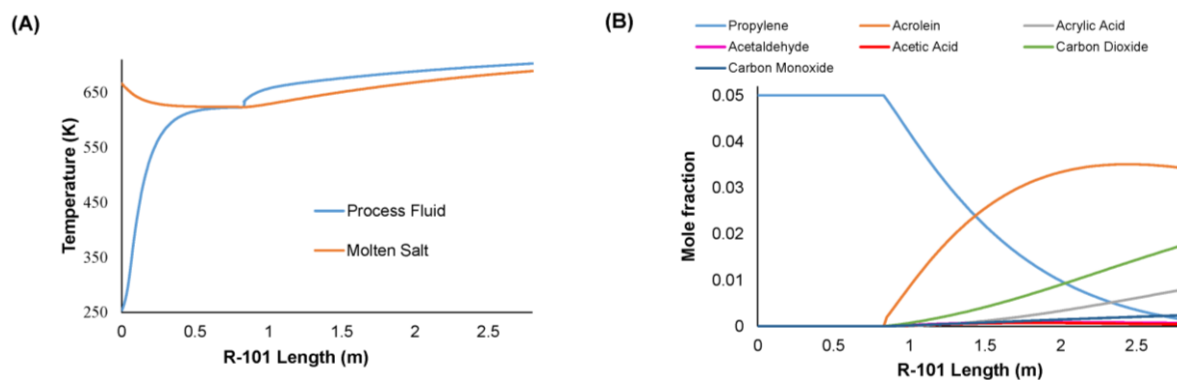

Figure 2: a) Temperature and b) composition profiles for the propylene oxidation reactor R-101, showing inert preheating and reaction zones.

Dilution of catalysts with solid inerts is a widely practised means of mitigating hot spots in wall-cooled reactors. The catalyst distribution may be used to influence the reactor temperature. Substantial difficulty in convergence of reactor R-102 occurred due to the inability of the varying coolant and reactor geometry to maintain the reaction within the temperature range of 533 to 573 K due to the highly exothermic nature of the reaction kinetics. Inefficient heat transfer can be controlled using inerts since the reaction rate in the inert section is reduced thereby reducing the heat generated by the exothermic reactions. As an initial estimate, 25 % inerts were assumed to be used in R-102 to determine the extent to which the reactor temperature would be controlled. In addition, the hotspot was required to be mitigated since the reaction is prone to rapid runaway with minor coolant variations. Figures 3 and 4 illustrate the results of sensitivities conducted on varying quantities of inerts in an attempt to control the reaction temperature range as well as prevent the formation of the hotspot. Since the

reaction could still not be optimally controlled, a cold shot of air was used to collectively cool R-101 effluent to the required temperature of 533 K whilst ensuring that the feed stream contained sufficient inert gases to control the reaction rate in R-102 and hence remove the formation of the hotspot. These results are illustrated by the thermal and composition profiles presented in Figure 5. The use of these strategies, together with the optimization procedure presented in the previous section, resulted in a reduction in required cooling fluid flow of 34 %, translating to an energy saving of approximately 14 % based on pumping and utility cooling costs, taking into account the steam credit usually obtained from the spent cooling fluid in a waste heat boiler.
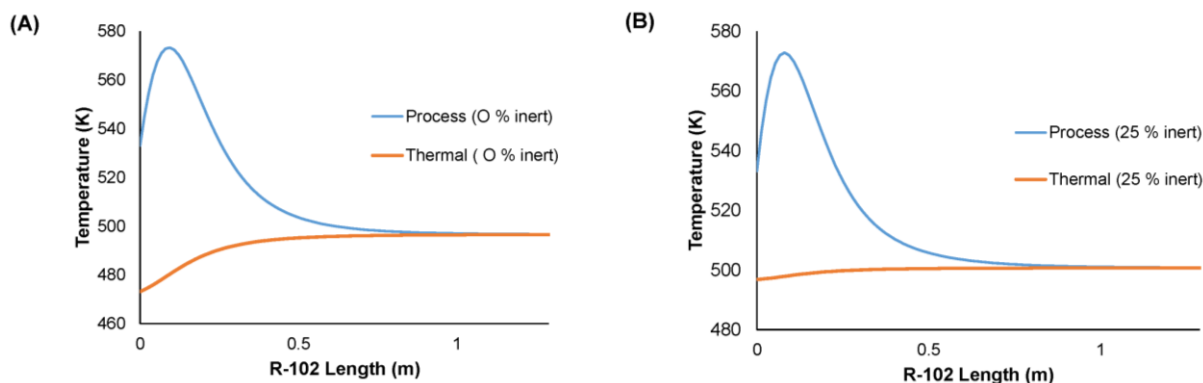

Figure 3: Temperature profile in base case design of acrolein oxidation reactor R-102 with a) 0% inerts and b) 25% inerts.
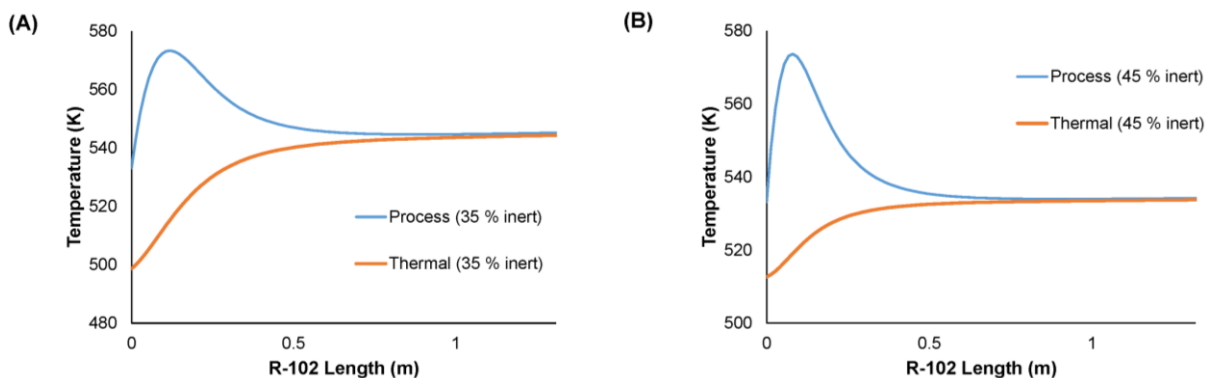

Figure 4: Temperature profile in base case design of acrolein oxidation reactor R-102 with a) 35 % inerts and b) 45 % inerts.
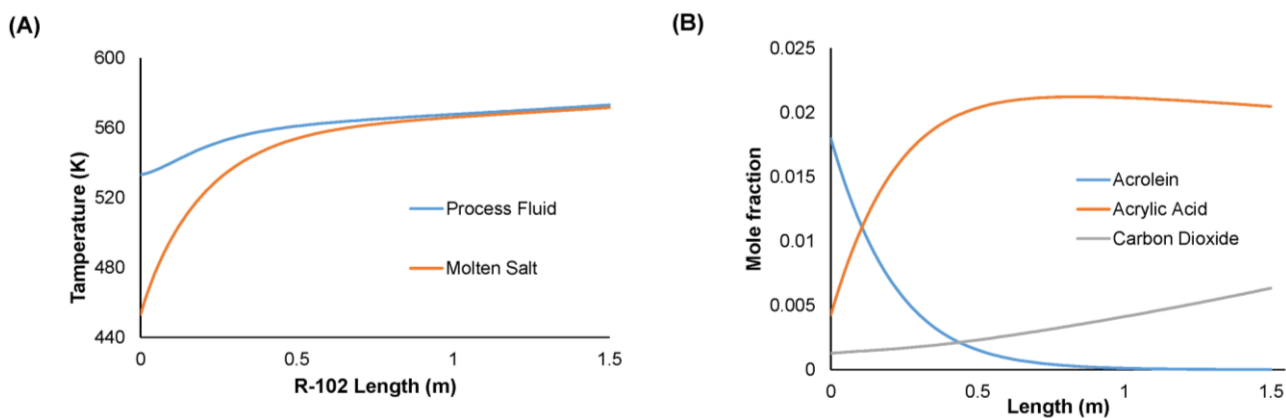

Figure 5: a) Temperature and b) composition profiles for the acrolein oxidation reactor R-102, employing cold-shot cooling and dilution of the inlet stream with air to mitigate hot-spot formation.

4. Conclusions

The design of a multitubular fixed bed reactor train for the production of acrylic acid involves simultaneous consideration of various influencing parameters, including shell side heat transfer, shell side pressure drop, tube-side hot spot formation, tube side pressure drop, catalyst interfacial gradients and selection of inlet conditions. For both the propylene oxidation reactor (R-101) and acrolein oxidation reactor (R-102), the heat transfer fluid flow rate affected the minimum temperature the most whilst the maximum temperature was affected by the heat transfer fluid inlet temperature the most. Some of the energy carried in the molten salt recycle was utilized to preheat the feed to reactor R-101 by including an inert packed zone of approximately 0.8 m at the front of the reactor. This eliminated the need for a separate preheating exchanger before the reactor. Allowing for some reduction of the molten salt temperature at the front end of reactor R-101 also limited the overall temperature rise in this unit for both the process and thermal fluid. Dilution of catalyst was investigated as a means of regulating the bed temperature in the acrolein oxidation reactor R-102. However, employing solid inerts up to 45 % did not significantly reduce the temperature rise or peak temperature in the reactor. An alternative strategy of cold air injection at the inlet of the reactor was successful in mitigating hot spot formation and allowing for a gradual increase in process side temperature, albeit with a higher final temperature than in the case of catalyst bed dilution. The accurate representation of the process performance on the ASPEN Plus® platform allowed for probing of alternative energy utilization strategies.

References

Asif, M., 2013, Conversion enhancement of fixed-bed reactors using two-dimensional hollow cylindrical catalyst pellet, International Journal of Chemical Reactor Engineering, 11, 159-168.

Beerthuis, R., Rothenberg, G., Shiju, N.R., 2015, Catalytic routes towards acrylic acid, adipic acid and ε-caprolactam starting from biorenewables, Green Chemistry, 17, 1341-1361.

Borio, D.O., Gatica, J.E., Porras, J.A., 1989, Wall cooled fixed bed reactors: Parametric sensitivity as a design criterion, AIChE Journal, 35, 287-292.

Estenfelder, M., Lintz, H.G., 2002, Simultaneous determination of reaction kinetics and oxygen activity in single-phase oxidic catalysts and their mixture during partial oxidations, Journal of Catalysis, 209, 177-185.

Jiang, B., Hao, L., Zhang, L., Sun, Y., Xiao, X., 2015, Numerical investigation of flow and heat transfer in a novel configuration multi-tubular fixed bed reactor for propylene to acrolein process, Heat and Mass Transfer, 51, 67-84.

Nojiri, N., Sakai, Y., Watanabe, Y., 1995, Progress in Chemical Process Development in Japan, Catalysis Reviews: Science and Engineering, 37, 145-178.

Petrescu, L., Fermeglia, M., Cormos, C.C., 2016, Life cycle analysis applied to acrylic acid production process with different fuels for steam generation, Journal of Cleaner Production, 133, 294-303.

Rase, H.F., 2000, Handbook of commercial catalysts: Heterogeneous catalysts, CRC Press, Boca Raton, USA.

Redingshofer, H., Krocher, O., Bock, W., Huthmacher, K., Emig, G., 2002, Catalytic wall reactor as a tool for isothermal investigations in the heterogeneously catalyzed oxidation of propene to acrolein, Industrial and Engineering Chemistry Research, 41, 1445-1453.

Redlingshofer, H., Fischer, A., Weckbecker, K. H., Emig, G., 2003. Kinetic modelling of the heterogeneously catalyzed oxidation of propene to acrolein in a catalytic wall reactor, Industrial and Engineering Chemistry Research, 42, 5482-5488.

dos Santos, R.O., Santos, L.S., Prata, D.M., 2018, Simulation and optimization of a methanol synthesis process from different biogas sources, Journal of Cleaner Production, 186, 821-830.

Sinnott, R.K., 2005, Chemical Engineering Design, Butterworth-Heinemann, Oxford, UK.

Sou, M., Zhang, H., Ye, Q., Dai, X., Yu, H., Li, R., 2015, Design and control of an improved acrylic acid process, Chemical Engineering Research and Design, 104, 346-356.

Tripodi, A., Compagnoni, M., Martinazzo, R., Ramis, G., Rossetti, I., 2017, Process simulation for the design and scale up of heterogeneous catalytic process: Kinetic modelling issues, Catalysts, 7, 159.