Process-Design Intensification – Direct Synthesis of Adipic Acid in Flow

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Micro process technology and flow chemistry have given a strong push to continuous chemical manufacture. This was based on the so-called transport intensification field which considerably improves mass and heat transfer given by the miniaturization of flow dimensions. The emerging second chemical intensification field uses highly intensified, unusual and typically harsh process conditions to boost micro-processing (Hessel et al., 2012). Beyond these, a third Process-Design Intensification Field heads for integrated and simplified flow process design in a more holistic picture. Chemical and process-design intensification constitute Novel Process Windows. As first-hour demonstration example for the latter, the direct oxidation of cyclohexene with hydrogen peroxide for adipic acid synthesis provides an innovative alternative to the industrial technologies currently being used. Profound simplification of the process scheme leads to fewer unit operations enabling reduction of investment cost, although the microreactor costs are higher than those of the batch reactor. Through simplification or elimination of energy intensive separation units energy consumption is reduced significantly. This leads to lower utility requirement and lowers the operating cost.

1. Introduction

The chemical industry is under pressure due to strong competition with emerging markets especially in Asia, increasing product requirements demanded by the customer and increasing environmental and social legislations. Therefore there is a strong demand for sustainable and cost -efficient solution. This cannot be solved anymore by process optimization since current processes are performed efficiently. A step change improvement can be achieved by use of entirely new apparatuses and new approaches in processes that is brought by process intensification (Stankiewicz and Moulijn, 2000). Process Intensification presents a set of often radically innovative principles in process and equipment design, which can bring significant benefits in terms of process and chain efficiency, capital and operating expenses, quality, wastes, process safety, and more as defined by the European Roadmap for Process Intensification (SenterNovem, 2007).

Micro process technology form a major direction within process intensification (Charpentier, 2007). It enables a revolutionary type of processing through entirely new and innovative equipment in continuous flow mode (Hessel et al., 2009). Microstructured equipment increase mass and heat transfer, minimize back-mixing and enable better temperature and residence time control. In this way the yield and selectivity of chemical reactions can be remarkably increased (Hessel et al., 2005b, Noel and Buchwald, 2011). They can also enable simplification of the process flow. The small hold-up reduces the damage potential of explosions making them safer and environmentally more benign (Hessel et al., 2005a). There is a paradigm change in chemical processing with micro process

technology: the equipment is adapted in order to reveal the intrinsic kinetics by adjusting to the demands of the chemical reaction itself (Schwalbe et al., 2005, Noel and Buchwald, 2011).

Process intensification through micro process technology allows reaching processing far from state of the art. Novel Process Windows aim at the intensification of the intrinsic reaction kinetics performed on micro scale under harsh process conditions and continuous flow operation as well as at the exploitation of synergetic effect in the integrated systems (Hessel, 2009). Synergy of micro dimensions and harsh operating conditions results in the three step intensification within a reaction system: transport, chemical and process-design intensification. Transport intensification has been vastly demonstrated (Hessel et al., 2011). Chemical intensification uses highly intensified, unusual and typically harsh process conditions to boost micro-processing (high-T, high-p, high-c, safety) and is used increasingly. Process-design intensification is a new field in micro processing and it considers a completely new and simpler process design. Figure 1 shows all the six major process intensification pathways for Novel Process Windows (Kralisch et al., 2012, Hessel et al., 2012).
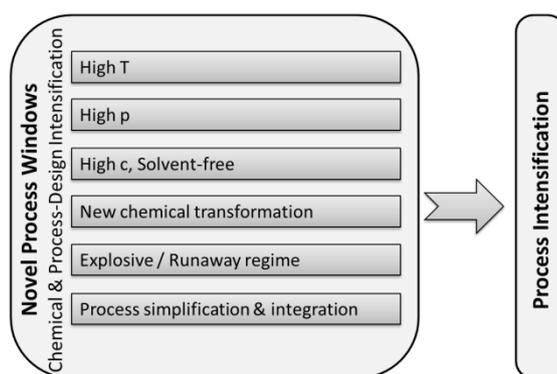

Figure 1: Major process intensification pathways for Novel Process Windows

Process-design intensification can make use of transport and chemical intensification when transferring these to full-process level and thus making the impact holistic. Higher selectivity and lower solvent loads can lead to reduction in separation requirements and equipment sizes. A step change improvement can be realized via bringing new chemical transformations such as direct synthesis on a full-process level. Such direct chemistries have the potential to reduce the cascades of separation units considerably. Other chances for process simplification are provided by the exchange of heating/cooling units through achieving room temperature processing, and by reducing expenditure for process control units due to self-control/-sustainment or higher degree in process stability (Hessel et al., 2012). In a more advanced step integrated reactors will partly replace consecutive arrangement of otherwise separated units due to the compactness of the basic elements within the units and the high speed of processing.

2. Direct Synthesis of Adipic Acid in Flow

The process-design intensification through microreactors and flow processing is new in literature. The authors have started for the first time to investigate this on one reaction example (Hessel et al., 2012): the direct synthesis of adipic acid which is an important chemical intermediate for the nylon industry. About 80 % of worldwide adipic acid consumption is used for the manufacture of Nylon 6,6 fibers and resins. It is also largely used in the manufacture of polyesters for use in plasticizers, lubricants and in a variety of polyurethane resins (Musser, 2005). Without exception, current commercial production processes for adipic acid are carried out in two stages. The first step involves the production of so-called KA oil (a mixture of cyclohexanone, the ketone or K component, and cyclohexanol, the alcohol or A component). The second stage involves oxidation of the KA oil to adipic acid with an excess of strong nitric acid in the presence of copper and vanadium catalysts where adipic acid is obtained in 92-96 % yield (Oppenheim and Dickerson, 2003). Figure 2 shows current industrial processes for the synthesis of adipic acid with solid lines.
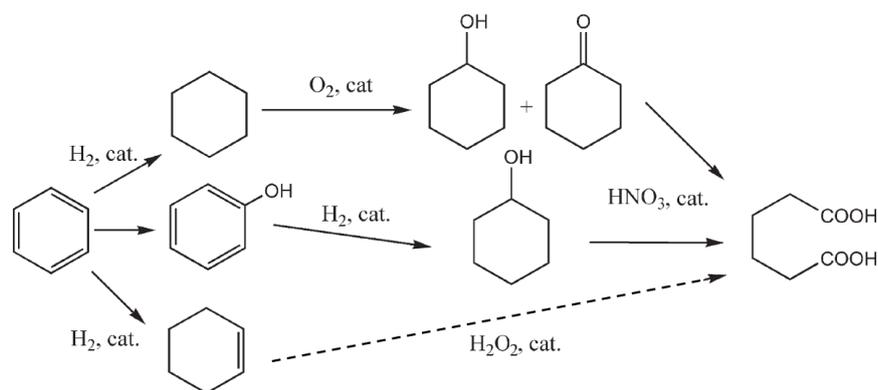
Figure 2: Processes for the synthesis of adipic acid (solid lines: current industrial processes, dashed line: direct synthesis alternative)

The cyclohexanone and cyclohexanol can be produced by different methods. By far, the most common route is the air oxidation of cyclohexane. Selectivities vary inversely with conversion. In order to promote the selectivity (85-90 %), low conversion levels per pass are achieved (4-8 %). Accordingly, the unconverted cyclohexane must be recovered by distillation and recycled. Phenol hydrogenation is an alternative commercial route. However, because of the relatively high cost of this raw material, cyclohexane-based processes are used predominantly (Oppenheim and Dickerson, 2003). All these approaches include two steps, first benzene is either hydrogenated to cyclohexane or oxidized to phenol. Then in the second step these are converted to cyclohexanol and cyclohexanone.

In the second stage of converting KA oil to adipic acid by nitric acid oxidation, the high concentration (50-60 wt %) and large consumption of nitric acid causes serious problems, since nitric acid is highly corrosive. Moreover, nitric acid oxidation produces significant quantities of nitrous oxide (N_2O) and NOx (NO, NO_2, and higher oxides) gases. The N_2O emission from this process causes global warming and corresponds to 5 to 8 % of the total amount released by man worldwide (Reimer et al., 1994).
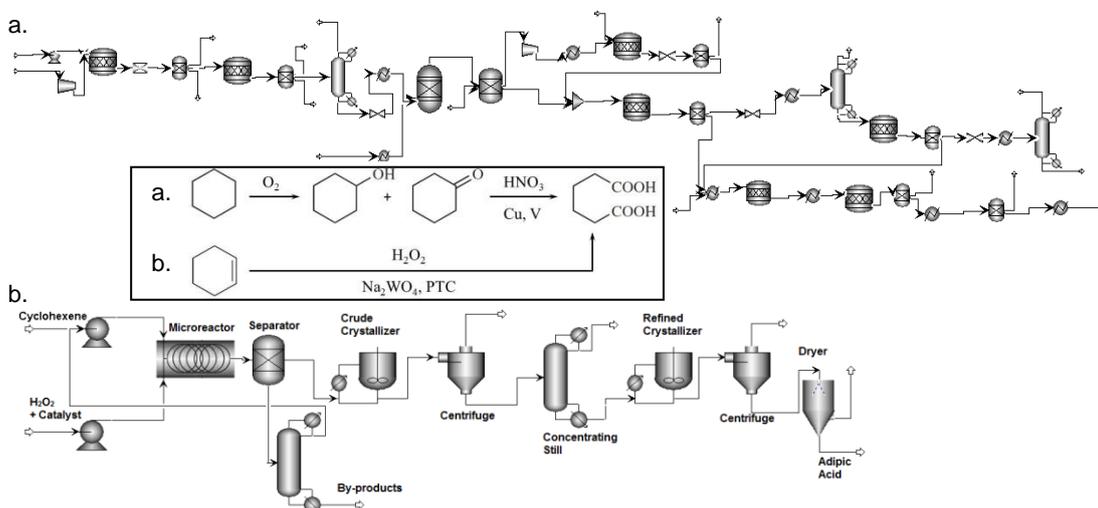

Figure 3: Flow schemes of adipic acid synthesis routes commercial 2-step (a.) vs. direct route (b.)

Research effort has thus been concentrated to search for an economically viable, practical (single stage, without high amount of recycle) process avoiding N_2O production, and thus use of nitric acid. Air oxidation of KA oil as well as one-step air oxidation of cyclohexane to adipic acid is attractive and heavily researched. However, the yield achieved is lower when compared with nitric acid oxidation and the solvent used (acetic acid) is highly corrosive (Onopchenko and Schulz, 1973).

Recently, direct oxidation of cyclohexene to adipic acid by 30 % hydrogen peroxide (H_2O_2) with Na_2WO_2 and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as a phase-transfer catalyst has been reported (see Figure 2 dashed line) (Sato et al., 1998). This aqueous, organic biphasic reaction enables high yield (93 %) under conditions that are entirely free of organic solvents and halides. There are environmental advantages of using H_2O_2 as oxidant claimed, since water being the sole expected by-product and thus achieving clean and safe operation that is among the green chemistry approaches of an industrial synthesis.

Use of microreactor technology for this route would enable to overcome limits in interfacial transfer, to safely handle hydrogen peroxide, to explore new, harsher process chemistries, and to test for better selectivity at much reduced reaction times (transport and chemical intensification fields).

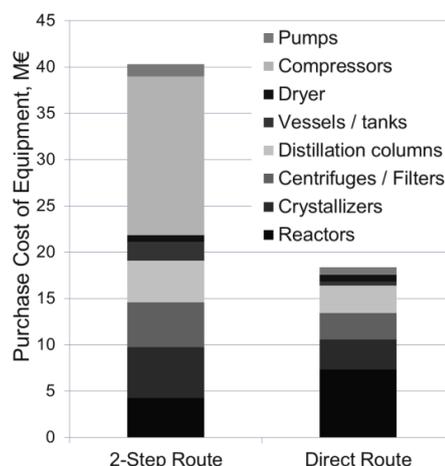| Commercial (2-Step) Route		Direct Route	
List of Equipment	Cost Estimates M€	List of Equipment	Cost Estimates M€
Pump	1.00	Pumps	0.80
Compressor	7.50	Oxidation reactor	7.30
Oxidation reactor/s	1.25	Phase separator	0.40
Decomposition reactor	1.00	Crude crystallizer	1.75
Neutralization vessel	0.80	1st Centrifuge/Filter	1.60
Distillation	1.25	Concentrating still	1.50
+ Pump	0.40	Refined crystallizer	1.50
Oxidation reactor/s	1.25	2nd Centrifuge/Filter	1.25
Bleacher	0.80	Dryer	0.75
Compressors	9.60	Distillation	1.50
NOx absorber	0.75		
Crude crystallizer	2.25		
1st Centrifuge/Filter	1.95		
Redissolving tank	0.45		
Refined crystallizer	1.50		
2nd Centrifuge/Filter	1.25		
Dryer	0.75		
Concentrating still	1.50		
Purge crystallizer	1.75		
3rd Centrifuge/Filter	1.60		
Distillation	1.75		
Total Purchase Cost	**40.30**		**18.35**

Figure 4: Cost of equipment comparison of 2-step vs. direct route (Hessel et al., 2012)

In order to compare the commercial route (2-step air and nitric acid oxidation of cyclohexane) with the direct synthesis route, process simulations were done. The commercial route was modelled with data from the industrial production process (see Figure 3a) and the direct route is modelled as a continuous process with microreaction technology (see Figure 3b). As can be seen from the process flow diagrams of the two routes, the direct route leads to a more compact plant design. There is requirement of less process units: only one reactor is needed and energy intensive separation units are either eliminated or simplified.

For further comparison of the routes cost analysis was carried out. The study was started by estimating the capital investment and for that purchased cost of equipment present in the routes was determined using sizing information from process simulation. It was demonstrated that with the direct route in flow the total purchase cost of equipment can be cut approximately in half (see Figure 4).

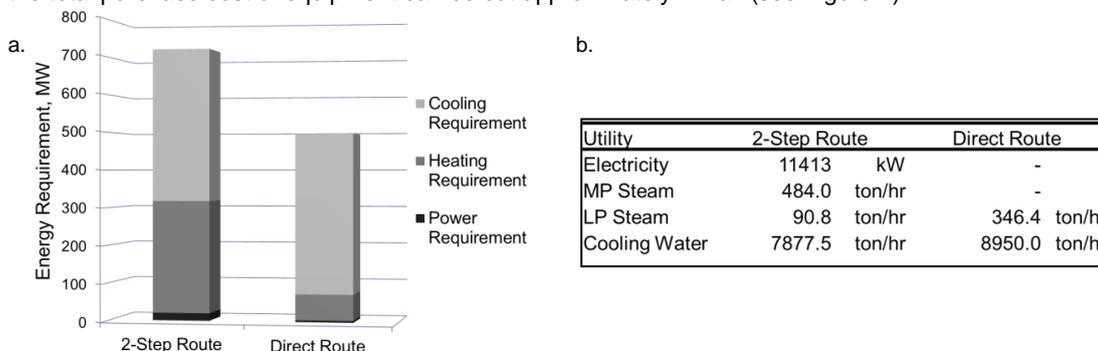| Utility	2-Step Route		Direct Route	
Electricity	11413	kW	-	
MP Steam	484.0	ton/hr	-	
LP Steam	90.8	ton/hr	346.4	ton/hr
Cooling Water	7877.5	ton/hr	8950.0	ton/hr

Figure 5: Energy consumption (a.) and utility requirement (b.) comparison of 2-step vs. direct route

In the 2-step route there is requirement of costly compressors to compress the air to be fed into the oxidation reactor. It has been seen that elimination of the compressor in the direct route with the use of liquid H_2O_2 as oxidant has a big impact in terms of capital investment. With the reduction in number of steps in synthesis lead to less number of downstream units (separator vessels, distillation columns, crystallizers and centrifuges). Correspondingly the total cost of equipment for separators has decreased in comparison to the 2-step route. However, there is an increase in cost for the more advanced flow reactor shifting the plant footprint from separation dominated to reaction dominated.
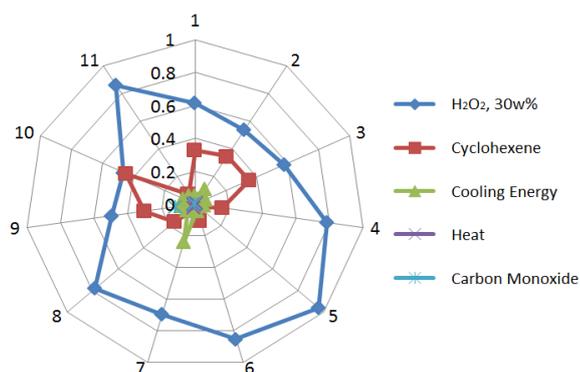

Figure 6: Process modules and their influence concerning different LCA results.

As a next step operating cost considerations has been started. To determine utility requirements for the two routes energy consumption analysis was carried out. The power, heating and cooling requirements for the equipment were determined using results of process simulation. Owing to the simplified process design, total energy consumption for the direct flow process was found to be about 30 % lower than that for the 2-step commercial process (see Figure 5a). It is important here that the energy intensive separation units i.e. distillation are either eliminated or simplified. The energy consumption values were converted to the utility requirements in terms of electricity to supply auxiliary equipment, medium pressure (MP) or low pressure (LP) steam for supply of heating and cooling water for supply of cooling. It was seen that the cost of utility that is an item in operating cost can be reduced with the use of direct route (see Figure 5b) due to use of lower cost LP steam instead of MP steam and elimination of electricity requirement with atmospheric pressure operation and use of no vapour streams.

Besides cost analyses some first estimations of environmental impacts of the direct route have been done. The Life Cycle Assessment (LCA) methodology offers to assess the environmental impacts associated with processes. For this purpose, the calculated mass and energy flows are assigned to different environmental impact categories. This was performed for the process modules of the direct route with 11 of these categories (see Figure 6) to analyse their impact on the environment. It was seen that H_2O_2 has the biggest effect among others. Major effects are on toxicity and land use; this is larger related to the less sustainable Anthraquinone making process, showing that the green assignment is a complex matter and seen differently when viewed from cradle to grave. Further analysis will be done to compare the environmental impact of the direct route with the 2-step route.

3. Conclusion

The investigation of process-design intensification through microreactors and flow processing is started here for the first time. It is exemplified at a currently investigated process example of industrial relevance: direct oxidation of cyclohexene with hydrogen peroxide for adipic acid synthesis. In order to compare the 2-step commercial route with the direct synthesis route in flow process simulations are done. It is demonstrated that the direct flow process leads to more compact plant design owing to the need of much less process apparatus (one reactor, less number of downstream units). Further analysis in terms of cost, energy and environmental impacts has begun. The capital investment is very much reduced as seen from the cost of equipment calculations, although the microreactor costs are higher than the batch reactor. The utility requirement which is an item used in operating cost estimation is also reduced significantly found from the reduced energy consumption with the simplification or elimination of energy

intensive separation units. Evaluation of the direct route in terms of environmental impact has also been started. While transport intensification nearly always lead to CAPEX cost increase and can decrease OPEX costs, it is process-design intensification which can reduce CAPEX costs – thus, lowering the main decision barrier in the management of chemical industry towards new technologies.

4. Outlook

Further analysis will be carried out to analyse process-design intensification regarding cost, energy and environment. On another hand, the author studies the implementation of flow units into modular plant environments such as container plants developed by Evonik Industries. A detailed economic evaluation comparing conventional and modular plants has just been finished using cash-flow analysis and Net Present Value (NPV) calculations. This is part of a separate paper which is ready for submission (in journal Green Processing and Synthesis). It will be highlighted that the container plants have high potential to achieve greater economic return with lower investment cost and shorter planning and construction period that boosts NPV. It is found container plants and microreactors can be synergistic in costs.

Acknowledgements

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