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Techno-economic assessment of the production of phthalic anhydride from corn stover

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ABSTRACT

Phthalic anhydride is used worldwide for an extremely broad range of applications spanning from the plastics industry to the synthesis of resins, agricultural fungicides and amines. This work proposes a conceptual design of a process for the production of phthalic anhydride from an agricultural residue (i.e. corn stover), energy integration alternatives as well as water consumption and life cycle greenhouse emissions assessment. The techno-economic and financial appraisal of the flowsheet proposed is performed. Results show how the valorization of all the carbohydrate-rich fractions present in the biomass as well as energy savings and integration is crucial to obtain an economically viable process and that it is in principle possible to produce renewable phthalic anhydride in a cost-competitive fashion with a lower impact on climate change compared to the traditional synthetic route.

1. Introduction

World phthalic anhydride (PA) demand is mainly driven by end-use applications such as phthalates-based plasticizers (62%), resins (38%, e.g. alkyd and UPE resins) and, to a lesser extent, dyes (mcgroup, 2015). Despite emerging trends of plasticizers manufacturing to become increasingly phthalate-free, the PA market currently accounts for more than 3 million tonnes per year and is expected to grow at about 2.4% per year in the near term (IHS, 2015).

Until the 1960s PA was based on coal-tar naphthalene oxidation processes. In the 90s, most of the PA was obtained from o-xylene, which can be separated from mixtures of xylenes containing roughly one third o-xylene and two thirds p-xylene. Although most of the PA production plants typically envisage possibilities of switching between the two feedstocks, the manufacturing costs are necessarily linked to fossil (mostly oil) price fluctuations. As such, a renewable route to PA would be highly encouraged as a first step towards a completely bio-based production of polyesters or polycarbonates (Winkler et al., 2015).

The development of chemicals manufactured from renewables (i.e. bio-based chemicals) has been receiving an increasing interest not only due to environmental policies (at both national and international levels) but also due to initiatives of private companies (like Cargill and BASF) (Golden and Handfield, 2014). The emerging bioeconomy growth is currently led by the bio-plastics sector but is expected to soon include specialty chemicals up to a significant extent (Arundel and Sawaya, 2009). The replacement of petroleum-derived products with bio-based ones is a promising answer to energy security and climate change issues. As a matter of fact, a large number of potential applications of biomass to produce bulk and niche chemicals have already been disclosed by chemistry and biotechnology researchers (EC, 2006) but concerns regarding the technical and practical feasibility of large-scale biorefining infrastructures still hinder the expansion of these systems.

Bio-ethanol has received considerable attention as a basic chemical and fuel additive. The extensive research on bioethanol has revealed that process intensification is essential to cut the production costs and ensure process viability. He and Zhang (2011) designed and optimised a thermo-chemical process for ethanol production where biomass wood chips were dried and gasified. The syngas produced was then cleaned and converted into alcohols. Ethanol and a mixture of higher alcohols were purified and sold. He and Zhang (2011) assessed the process in

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terms of carbon and CO conversion, ethanol yield, synthesis selectivity and ethanol production cost. The results showed that major contributions to the production cost are from biomass feedstock and syngas cleaning. Cost-competitive ethanol production can be realized with optimal systematic conguration and heat integration as well as high value by-products.

In the biorefining context, though, only a limited number of studies have proposed rigorous techno-economic assessments of selected bio-based chemicals. Trippe et al. (2011) proposed a techno-economic assessment of biomass-derived slurry (bioliq) in a potential industrial scale entrained flow gasifier. They emphasised that the role of syngas in future bioeconomy allowed a wide variety of fuels and chemicals using specific catalysts, and that feedstock cost mainly affected production costs.

The integration of lactic acid production in the sugarcane-based biorefinery was targeted by Sikder et al. (2012). Lammens et al. (2012) have developed a techno-economic feasibility analysis of bio-based products derived from glutamic acid.

Haro et al. (2013) proposed the conceptual design of 12 alternatives developed around the concept of an indirect ethanol production biorefinery using dimethyl ether (DME) as an intermediate. They studied the polygeneration of high-value chemical products (methyl acetate and H_2), liquid transportation fuels (ethanol and DME) and electricity. For the market price of products the internal rate of return was always above 20% for process concepts based on DME carbonylation. In the most profitable scenario, a rate of return of 28.74%, was obtain where methyl acetate, DME and power were produced.

Cok et al. (2014) proposed an energy and greenhouse gas emissions assessment of bio-based succinic acid obtained from carbohydrates. Kim et al. (2014) performed a conceptual design and studied the economics of ethanol production using starch and lignocellulosic biomass as starting feedstocks. They showed that the economics of the system were significantly improved when the efficiency in the use of biomass was augmented. They combined several pretreatment processes (i.e. the dilute acid and aqueous ammonia pretreatments), and proposed a process of waste media containing xylose for the production of 7-aminocepha-losporanic acid. Tang et al. (2014), finally, explored in their review the role of GVL (γ-valerolactone), obtainable by selective hydrogenation of lactic acid and its esters, as a solvent for producing chemicals and building-block for generation biofuels. A cost-effective process for producing lactic acid from lignocellulosic biomass was shown as the real bottleneck for the GVL production in a large scale, because of its strong acidity and low volatility.

A renewable route to PA was investigated at a lab scale by Mahmoud et al. (2014) using biomass-derived furan (F) and maleic anhydride (MA). This represented a promising avenue for the production of PA from diverse routes compared to the traditional fossil-based one at the same time using residual feedstock (the so-called second generation biomass) whose exploitation would not interfere with the food supply chain. In this work, the originally developed conceptual design proposed by Giarola et al. (2015) for the production process of PA from corn stover, is extended proposing pinch analysis and energy integration solutions. Additional product sales are also modelled as a means to improve the profitability of the system (levulinic, maleic anhydride and formic acid, i.e. LA, MA, FA). The full techno-economic assessment, including economic and cash flow analyses as well as the water consumption and greenhouse gas (GHG) emissions appraisal of the process are presented.

2. Materials and methods

2.1. Gas-phase oxidation

PA is produced via the oxidation reaction occurring at about 360–390 °C (Lorz et al., 2012) of:

- o-xylene, with a heat of reaction between 1300 and 1800 kJ/mol of o-xylene and expected yields of 110–112 kg PA/100 kg o-xylene
- naphthalene, with a heat of reaction of 2100–2500 kJ/mol and yields usually not exceeding 98 kg PA/100 kg naphthalene; carbon dioxide is a co-product.

The traditional source for PA production was coal-tar naphthalene, which could be available at adequate purity only at high costs. Recently, the PA manufacturing has shown a shift towards o-xylene use, for the more attractive yields, availability and cost. As a major drawback, the process economics became more exposed to the main feedstock price variations as well as the high volatility of mixed xylenes in the international market (ICIS, 2015). In order to hedge this risk, some plants allow o-xylene-naphthalene switching or include a xylene separation plant.

The first patent (BASF in 1896) used concentrated sulphuric acid in the presence of mercury salts to perform the oxidation, but the major advancement in PA manufacturing occurred when the first vapour-phase process spread across the world with the development of highly selective catalysts based on vanadium pentoxides.

When o-xylene is the feedstock, it is first vaporized, mixed with hot air and passed through a fixed-bed tubular reactor where the oxidation takes place. The exothermic heat is removed by a molten salt bath circulated around the reactor tubes and transferred to a steam generation system.

When a naphthalene-based feedstock is used, vaporized naphthalene and compressed air are transferred to a fluidized bed reactor and oxidized in the presence of a catalyst. The cooling tubes transfer the exothermic heat from the catalyst bed to produce high-pressure steam.

The reactor effluent gases are filtered to recover the catalyst, precooled and passed through a liquid condenser, first, and to a switch condenser system, then, where the PA is condensed on the finned tubes as a solid. The switch condensers are cooled by a heat-transfer oil in an automated switching cycle: during the cooling cycles, PA crystals form while, during the heating cycle, the deposited PA is melted and collected from the condenser tubes in a storage tank. The exhaust gases still contain byproducts and small quantities of PA and must be cleaned by scrubbing with water, or catalytically or thermally incinerated. If scrubbing with water is employed, it is possible to concentrate the maleic acid, and, from the scrubbing solution maleic anhydride. The crude liquid is transferred to a continuous thermal/chemical treatment system, which converts the phthalic acid formed into the anhydride, then purified (99.8% wt.) in a continuous two-stage vacuum distillation system.

Current industrial plants exhibit a good variety of technological solutions operating at different ranges of o-xylene loadings (from 80 g/m^3 (STP) in the Alusuisse - Ftalital LAR (low air ratio) process, up to 105 g/m^3 (STP) in the BASF process).

2.2. A novel synthesis to PA based on biorenewables: input assumptions

In this work, a generic, simplified PA production process (displayed in Fig. 1) using corn stover as raw material was developed and simulated by means of a process simulator (Aspen Plus^{TM}). An energy optimisation was then performed according to the principles of the pinch analysis. An environmental appraisal of the GHG emissions of the process using a life cycle approach was also conducted. The water consumption of the system was also estimated. Table 1 reports