Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Conceptual process design of an integrated bio-based acetic acid, glycolaldehyde, and acetol production in a pyrolysis oil-based biorefinery

Caecilia R. Vitasari[a,*], *Geert W. Meindersma*[a], *André B. de Haan*[b]

[a] *Process Systems Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands*

[b] *(Biobased) Process Technology, Department of Chemical Engineering, Section Transport Phenomena, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands*

ARTICLE INFO

Article history:
Received 21 May 2014
Received in revised form 15 December 2014
Accepted 20 January 2015
Available online 28 January 2015

Keywords:
Conceptual design
Economic analysis
Acetic acid
Glycolaldehyde
Acetol
Biorefinery

ABSTRACT

This paper discusses the conceptual process design for the integrated production of bio-based acetic acid, glycolaldehyde, and acetol from forest residue- and pine-derived pyrolysis oils. Aspen Plus® and Aspen Process Economic Analyzer were used for process simulation and estimating the equipment cost, respectively. The process was designed at a capacity 200 kt pyrolysis oil per year, operating 8000 h annually, and involving extraction, distillation, and evaporation. It can isolate more than 99% of the glycolaldehyde and acetic acid and about two-thirds of the acetol present in the oils. In comparison with the forest residue-based process (21 M€), the pine-based process requires a higher capital investment of 23 M€ and a slightly higher production cost of 49 M€/a versus 48 M€/a, but can provide a higher revenue of 57 M€/a instead of 44 M€/a because pine-derived pyrolysis oil contains more acetic acid, glycolaldehyde, and acetol, which also makes it less sensitive to market price. Pine-derived pyrolysis oil is a preferable feedstock over forest residue-derived pyrolysis oil for an integrated chemical recovery process, whereas forest residue-derived pyrolysis oil generates no profit at an annual capacity of 50–600 kt oil. The economic feasibility of the designed process is highly dependent on the glycolaldehyde content of the pyrolysis oil.

1. Introduction

In a pyrolysis process, biomass feedstock is converted into liquid, char, and gas. Pyrolysis oil is a single phase mixture containing about 15–30 wt% water (Bridgwater and Peacocke, 2000; Oasmaa et al., 1997) and more than 300 oxygenated compounds such as acids, sugars, phenols, alcohols, hydroxyketones, and hydroxyaldehydes (Oasmaa et al., 1997; Piskorz et al., 1988). This rich composition makes it a valuable starting point for a thermochemical-based biorefinery where both conventional fuels and platform chemicals can be produced (Vitasari et al., 2011).

The conversion of pyrolysis oils into fuels have been widely explored, followed by process design and economic assessment (Brown et al., 2012; Gebreslassie et al., 2013; Ng and Sadhukhan, 2011; Wright et al., 2012). To date, there is no study on the techno-economic evaluation of the production of platform chemicals from pyrolysis oils.

Acetic acid, glycolaldehyde, and acetol are three future bio-based platform chemicals, which are available in a

* Corresponding author. Present address: BiCHEM Technology BV, Kastanjelaan 400, 5616 LZ, Eindhoven, The Netherlands. Tel.: +31 40 800 2320.
E-mail address: caecilia.vitasari@bichemtechnology.com (C.R. Vitasari).
http://dx.doi.org/10.1016/j.cherd.2015.01.010
0263-8762/

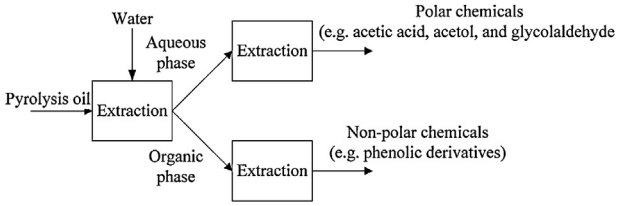

Fig. 1 – Indirect chemical isolation via water extraction.

considerable amount in pyrolysis oil. Wood-derived pyrolysis oil contains about 3–12 wt% acetic acid (Bridgwater, 2007; Sipilä et al., 1998), 5–13 wt% glycolaldehyde, and 0.7–7.4 wt% acetol (Diebold, 2003). Acetic acid is a common solvent and feedstock for producing vinyl acetate- and cellulose-derived polymers (Balser et al., 2004; Cheung et al., 2011). Glycolaldehyde is a food browning agent as well as a potential feedstock for producing renewable ethylene glycol via fermentation (de Haan et al., 2009). Acetol is an intermediate to produce propylene glycol, acrolein, propionaldehyde, acetone, and furan derivatives (Dasari et al., 2005). Besides, acetol is used to give flavour to food and milk (Mohamad et al., 2011).

Acetic acid and glycolaldehyde can be extracted directly from pyrolysis oil by reactive extraction with tri-*n*-octylamine (TOA) (Mahfud et al., 2008) and sodium bisulphite (Meindersma et al., 2009), respectively. However, both methods are not promising due to considerable TOA losses (Mahfud et al., 2008) and the stability of glycolaldehyde-bisulphite adduct complicates the product recovery (Meindersma et al., 2009).

For these reasons, another approach has been proposed to separate the target bio-based chemicals from pyrolysis oil (Fig. 1). Water addition to pyrolysis oil induces phase separation in which polar compounds are mainly isolated in the aqueous phase, while non-polar ones mostly remain in the organic phase. Hence, the complexity of pyrolysis oil is strongly reduced (Vitasari et al., 2011).

Based on literature data (Rasrendra et al., 2011) and our preliminary water extraction experiments, we have evaluated several possible integrated process configurations to isolate acetic acid and glycolaldehyde from pyrolysis oil via water extraction in Aspen Plus®. The studied process configurations were evaluated based on their process yields, energy consumption, and the estimated total annual costs (de Haan et al., 2011).

The evaluation shows that the designed process illustrated in Fig. 2 is the most promising process configuration. In this process 40 wt% TOA/2-ethyl-1-hexanol is used to extract acetic acid and glycolaldehyde simultaneously. This scenario provides the overall acetic acid and glycolaldehyde yields of 89.4% and 99.8%, respectively and has 2.5 times lower energy consumption compared to the separate acetic acid and glycolaldehyde isolation (de Haan et al., 2011).

Since it is promising to combine acetic acid and glycolaldehyde extraction, we further investigated two extraction schemes. The first one is the combined one-step extraction, where acetic acid and glycolaldehyde are simultaneously extracted with 2-ethyl-1-hexanol. The second method is the two-step extraction in which acetic acid is extracted with TOA/2-ethyl-1-hexanol at a concentration above 50 wt%, followed by the glycolaldehyde extraction with 2-ethyl-hexanol (see also Fig. 2). The combined one-step extraction was selected over the two-step extraction since it does not employ TOA (Vitasari et al., 2012a); hence, eliminates the complicated regeneration step by a coupling of temperature and diluent swings, which requires high temperature and energy consumption (Tamada and King, 1990).

Table 1 – Pyrolysis oil specifications (Vitasari et al., 2011).

	Forest residue-derived pyrolysis oil	Pine-derived pyrolysis oil
Elemental analysis:		
Carbon (wt%)	40.6	41.3
Hydrogen (wt%)	7.7	7.6
Nitrogen (wt%)	0.4	0.2
Oxygen (wt%)	51.2	50.9
Composition:		
Water (wt%)	25.6	24.9
Glycolaldehyde (wt%)	6.2	13.6
Acetic acid (wt%)	6.2	4.6
Acetol (wt%)	4.0	5.0
Furfural (wt%)	0.7	0.5
Furanone (wt%)	0.7	0.8
Levoglucosan (wt%)	1.7	1.6
Syringol (wt%)	0.3	0.1
Guaiacol (wt%)	0.2	0.6
LHV (MJ/kg)	15.3 (Oasmaa et al., 2010)	15.3 (Oasmaa et al., 2010)

This paper discusses the conceptual design of the combined one-step extraction process using 2-ethyl-1-hexanol as solvent. The designed process will be a part of a pyrolysis oil-based biorefinery. Therefore, the feedstock of the process is pyrolysis oil. It aims to produce pure compounds as the final products. In this paper, forest residue- and pine-derived pyrolysis oils were used as feedstocks. Unlike the previous conceptual design (de Haan et al., 2011), the process simulation used more elaborate experimental data (Vitasari et al., 2011; Vitasari et al., 2012a). The process design aimed to recover all acetic acid and glycolaldehyde with purity above 99%. Some acetol may be co-extracted in the extraction; hence, its recovery is also considered in the design.

The subsequent economic analysis evaluates the economic potential of both feedstocks. Furthermore, the profit sensitivity to plant capacity, annual operating hours, and market prices were assessed as well.

2. Methods

2.1. *Process design*

The process scheme was conceptually developed based on our laboratory experiments and our previous assessment on several simplified process scenarios (de Haan et al., 2011).

The conceptual process design was simulated in Aspen Plus® for a capacity of 200 kt pyrolysis oil per year, which is the same as that of the previous conceptual design (de Haan et al., 2011). The designed capacity was the same for both forest residue- and pine-derived pyrolysis oils since this designed process will be integrated to a pyrolysis oil-based biorefinery, which from the process point of view should be able to process various feedstocks.

The operating time was selected to be 8000 h per annum with an assumption that there is enough pyrolysis oil supply for the whole year operation. The compositions of the forest residue- and pine-derived pyrolysis oils and their low heating values (LHV) are depicted in Table 1.