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Recycling vs. reprocessing. Optimization of a gossypol production process

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ABSTRACT

Three processes to obtain GAA from the soapstock residue of oil refineries were compared in this work. The first process is the originally proposed by Dowd and Pelitire (2001. Ind. Crops Prod. 14, 113) in which the mother liquor from the last crystallization step still contains an appreciable amount of gossypol which is lost as a process residual stream. The second process recycles the mother liquor to the hydrolysis first step of the process, following the heuristic of the traditional process design procedure by Douglas (1988. Conceptual Design of Chemical Processes. McGraw Hill, New York, NY), which increases product yield. While the third process adds a new downstream processing line to reprocess the mother liquor. This last alternative renders a slightly lower product yield than Process 2 but requires a smaller investment cost, exhibiting the best economic performance.

The alternative of incorporating a recycle to reprocess unreacted material (in this case the bound gossypol present in the crystallization mother liquor) is the usual approach in traditional process design. However, in this particular study case, it does not succeed in rendering the process alternative with the best economic performance: the recycle stream flow impacts on the equipment sizes, increasing investment cost far beyond the alternative that adds smaller units to reprocess the mother liquor stream.

1. Introduction

Gossypol, (2,2′-bis(1,6,7-trihydroxy-3-5-isopropyl-8-aldehydonaphthalene) is a yellow pigment found in cotton (Gossypium) species. It constitutes 20–40% in weight of the gland responsible for pigmentation and accounts for 0.4–1.7% of the whole kernel (Dowd and Pelitire, 2001; Xi et al., 2009). Gossypol was first discovered as a crude pigment from cottonseed oil foot, a mixture of precipitated soaps and gums produced in the refining of crude cottonseed oil with sodium hydroxide.

Gossypol exists in a number of tautomeric and isomeric forms, depending on the position of methyl and hydroxyl groups in the carbon atoms adjacent to the binaphthalene. During cottonseed oil processing, gossypol and phosphatides are extracted together with triglycerides during solvent extraction. In the oil refining process, caustics are added so that free fatty acids, phosphatides and gossypol are separated from oil as a soapstock by-product (Kuk and Bland, 2002). Some evidence indicates that most gossypol exists as Schiff bases through the condensation between the aldehydic groups of gossypol and amino groups of proteins (Xi et al., 2009).

Kuk and Bland (2002)) studied the pH influence on the Schiff base resulting from the reaction of gossypol with phosphatidiletanolamine PE, which is the largest phospholipid present in oilseed soapstock. Their work found a strong dependence on pH in the formation of the Schiff base. This reaction is readily reversible by acidic hydrolysis in aqueous solution and can be chemically stabilized by reduction.

Gossypol has important biological properties in human health and toxic properties as animal feed. There are numerous studies about its biological activity such as antifertility

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Nomenclature

Subscripts

i	component
f	stream
eq	equipment
in(eq,f)	Stream f entering into equipment eq
out(eq,f)	Stream f exiting from equipment eq
outlight(eq,f)	*Light* stream f exiting from centrifuge eq
outheavy(eq,f)	Heavy stream f exiting from centrifuge eq

Variable

A	area of a heat exchanger [m^2]
CI	cost of Investment of an equipment [$]
D	diameter of a vessel [m]
Feed	volumetric inflow rate into the centrifuge [Gal/min]
H	height of a vessel [m]
P	power of a centrifuge [hp]
$Q_{(f)}$	mass flow rate of stream f [kg/h]
U	heat transfer coefficient [kcal/h m^2 °C]
Vol	volume of a vessel [m^3]
$W_{(i,f)}$	mass fraction of component i in stream f
X	fraction of the recycle incoming flow that is purged

Greek Symbols

ß	fraction of inlet MEK vaporized in the evaporator
μ	fraction of inlet (bounded) gossypol released in the hydrolysis
Φ	heat of vaporization of MEK

Definition

C1 and C2	tank of crystallization one and two
CE1 and	centrifuge of process
CEL	centrifuge washing
E1, E2 and E3	evaporator number
H1 and H2	hydrolysis reactors

(Coutinho, 2002) and anticancer activities, as well as inhibiting the growth of a variety of cell lines including breast, colon, prostate, and leukemia cells (Xi et al., 2009). Also, gossypol has antivirus activity that inhibits the replication of human immunodeficiency virus type 1 (Lin et al., 1989, 1993; An et al., 2012). Due to these biological properties, gossypol is a compound of interest for the pharmaceutical industry. Otherwise, this compound contributes to the toxicity of soapstock used as animals feed: gossypol would need to be removed from soapstock before adding it to poultry feed (Dumont and Narine, 2007).

The production of cottonseed oil in Argentina was 12,500 ton in year 2012 (CIARA, 2014), corresponding to a soapstock production of about 750 t/yr. Soapstock contains between 0.33 and 13% of gossypol (Dowd, 1996), considering an average of 7% its potential production rate is 50 t/yr. Thus, the locally available raw material would allow industrial scale production of gossypol.

There is abundant literature about isolating gossypol from this oil refining by-product. The basic processes consist of acid treatment to hydrolyze covalently bound gossypol, partitioning it into an organic phase, concentrating gossypol by vacuum evaporation of the organic solvent and finally crystallizing it as gossypol acetic acid (GAA), e.g. Dowd and Pelitire (2001), Pons et al. (1959), Jia et al. (2009).

The objective of this study was to optimize the structure of the process proposed by Dowd and Pelitire (2001). First, the hierarchical design concepts proposed by Douglas (1988) were applied, implementing the recycle of the liquid outlet stream from the crystallizer (the mother liquor) to the hydrolysis step of the process. This stream still contains about a 30% of the gossypol entering with the raw material. By recycling this stream the process product yield is increased, but also the size of the units involved in the recycle loop increase.

Afterwards we take a different approach by proposing to add a downstream reprocessing train, as an alternative to recycling. This alternative was analyzed and optimized. Finally, both processes were compared (mother liquor recycling and reprocessing) in order to select the GAA production process with the maximal economic performance.

2. Process modeling and optimization

We start considering the process proposed by Dowd and Pelitire (2001), who experimentally optimized its operating variables: reaction times, concentration of reactants, etc. as shown in Table 1, aimed at improving yield, subject to not jeopardize product purity.

The process consists of an initial hydrolysis with phosphoric acid, where the released gossypol is dissolved into the organic phase of methyl ethyl ketone (MEK). Then, the residual aqueous phase is washed with MEK to recover dissolved product. The stream containing gossypol is then concentrated by vacuum evaporation of MEK, and finally converted into GAA with the addition of glacial acetic acid and allowing time for crystallization.

The process is presented in Fig. 1, stream F1 is the soapstock feed: we adopted a base case flow rate of 100 kg/h with an average composition of 50% water, 38% free fatty acids FFA, 8.3% oil and 3.7% total gossypol (Dowd, 1996), while stream F2 is a 1.4 M solution of phosphoric acid in MEK. They are mixed in a hydrolysis reactor (H1) and afterwards the light phase is separated from the heavy one in the centrifuge (CE1). Stream F4 is the light phase containing most of the gossypol and stream F5 is the (aqueous) heavy phase, which is subjected to consecutive washes with MEK to recover the gossypol contained therein. E1 is an evaporator that concentrates the light phase producing stream F19 of recovered MEK. Stream F21 is glacial acetic acid and C1 is the crystallizer. Stream F24 is the process product: crystallized GAA (a crystalline inclusion complex containing an equimolar ratio of both) and F23 is the residual mother liquor.

The mathematical model consists of mass and heat balances, equipment sizing and cost estimations implemented with algebraic equations. Thus, it is a NLP (Non Linear Program) model that was implemented in GAMS (General Algebraic Modeling System). Product yields, flow rate ratios, concentrations, etc. were taken from Dowd and Pelitire (2001). A brief outline of the model follows.

The total and component mass balances are represented by Eqs. (1) and (2). Eqs. (3) and (4) describe the hydrolysis reaction, where μ is a conversion factor given as a mass fraction of the gossypol present in the raw material, taken from the literature (Dowd and Pelitire, 2001; Pons et al., 1959).