SHORT, NON-REFEREED PAPER

DEVELOPMENT OF REACTIVE EXTRACTANTS FOR THE ISOLATION OF CARBOXYLIC ACIDS

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Abstract

Bacteria and yeasts are extraordinarily selective converters of sugar to a variety of products (including alcohols and carboxylic acids). One of the biggest challenges for the implementation of any fermentation technology on a large industrial scale is the low concentration of the products obtained in the aqueous fermentation broth. Reactive extraction is a relatively new technology for the selective removal of fermentation products from mixtures. For this purpose, functionalised hydrophobic reactive extractants with certain physicochemical properties are required. Hence, this paper aims to introduce the concept of reactive extraction as a chemo-technological platform of the sugarcane biorefinery, and describes the possible functionalities and properties required for efficient reactive extraction, by using a carboxylic acid (levulinic acid) as a case study.

Introduction

Carboxylic acids are a group of versatile compounds that can provide building blocks for a very wide product portfolio. One carboxylic acid that has gained immense interest in a variety of applications, e.g. in chemical, pharmaceutical and food industries, is levulinic acid (De Jong *et al.*, 2012). The market size of levulinic acid has been predicted to increase by a factor of 150 within the next five years. Due to limitations in the petroleum-based production of chemicals, the production of carboxylic acids has shifted to fermentation and biorefinery based processes such as dehydration of C_6 and C_5 sugars (Murali *et al.*, 2017). The current innovations make use of renewable lignocellulosic feedstocks such as sugarcane, and are therefore foreseen to be sustainable over a long period of time.

However, one major drawback to the fermentation processes is the difficulty in isolating the very low concentrations of carboxylic acids produced (2-10 wt%). This is due to the fact that as the carboxylic acid concentration in the fermentation broth increases, the pH decreases, leading ultimately to an inhibition of the microorganism activity Hence, in order to improve process performance and reactor productivity, the accumulation of product in the fermentation phase needs to be limited. This can either be achieved by physically removing the product (extraction), or by a combination of reaction and extraction with a reactive extractant, as proposed herein.

Various techniques such as distillation, precipitation and solvent extraction, amongst others, have been investigated for their potential to extract carboxylic acids from aqueous solutions (Datta *et al.*, 2016; Joglekar *et al.,* 2006). Conventionally, carboxylic acids are recovered from fermentation by neutralisation with an inorganic base, leading to precipitation as a calcium salt. After separation by filtration, the resulting salt is acidified to recover the carboxylic acid. However, this method is costly as it creates problems in downstream operations (semi-batch filtration), and generates an

excess of solid waste in the form of calcium sulfate which presents disposal issues. Solvent extraction could be an alternative strategy for the recovery of carboxylic acids; however, due to the low selectivity achieved, distribution coefficients are prohibitively low (Clarke *et al.*, 2018). There is, therefore, a need to develop alternative routes to recover and isolate carboxylic acids. This draws attention to the concept of reactive extraction, where phase separation is enhanced by concurrent chemical reaction (Wasewar 2012).

It should be noted that numerous studies have reported the reactive extraction of carboxylic acids, proposing, in particular, the use of tertiary amines (e.g. Datta *et al.* 2015). However, from a chemical viewpoint, the use of amines is a neutralisation reaction, leading to similar problems as those encountered when neutralising with an inorganic base, as described above. Furthermore, amines are toxic and highly volatile and present serious environmental concerns. Hence, a different reaction type has to be considered to avoid these problems. For this purpose, alternative reactive extractants were developed and their application in reactive extraction have been investigated.

Strategy

For the development of reactive extraction systems, both their physical (allowing for the physical extraction into the extraction phase) and chemical properties (allowing the reaction step to take place) need to be considered. These will affect the overall mechanism, i.e. if extraction precedes reaction, this will also determine in which phase the reaction step occurs. Evidently, this will have an impact on the choice of extractor type and other downstream operations.

Firstly, the extraction step is governed by mass transfer dynamics and equilibrium conditions (Wasewar 2012). In order to achieve physical separation, the extractant must possess the following properties:

- Low mutual solubility between the extractant and the aqueous phase, and high selectivity for the product in order to reduce the number of separation stages and improve the final product purity;
- Low toxicity to reduce hazards of exposure for operating personnel and emissions into the environment;
- Large density difference between the extractant and aqueous phase to enhance settling;
- Low interfacial tension to facilitate phase dispersion, and, hence, improve mass transfer;
- High capacity for the product to allow for the utilisation of low solvent-to-feed ratios;
- Facile recovery to reduce the cost of the extractant and environmental impact arising from effluent treatment.

Secondly, for the reaction step, the extractant must bear a task-specific functionality where the reaction will take place, increasing both the capacity and selectivity of the process (Hong *et al.* 2001). In order to allow for simple regeneration of the reactive extractant, the reaction must be fully reversible.

In this work, esterification was thought to be an ideal reaction type to fulfil these requirements. In order to design a reactive extractant for the removal of carboxylic acids, a hydroxyl functional group was appended onto the extractant. It is clear that the same principle could be used for the reactive extraction of alcohols, such as butanol, if a reactive extractant with a carboxylic acid moiety was produced. As a result, the reactive extraction can be fine-tuned by selection of the functional groups on the extractant.

In this study, a versatile group of hydrophobic solvents with chemical structures that can be tailored to tune both the physical and chemical properties was developed (Stark 2016).

Figure 1 illustrates the proposed scheme for the reactive extraction process. The carboxylic acid produced by microorganisms in the fermentation broth will undergo an esterification reaction with the hydroxyl-functionalised extractant, thus enhancing mass transfer from the aqueous phase into the extractant phase. The phase separation will drive the fermentation towards higher conversions due to the reduction of end-product inhibition within the fermenter. Since esterification is a reversible reaction, stripping off the product from the extractant (via hydrolysis or transesterification) will then allow for the regeneration of the extractant and reuse in the extraction process. This reactive extraction system can thus facilitate the establishment of integrated biorefineries.

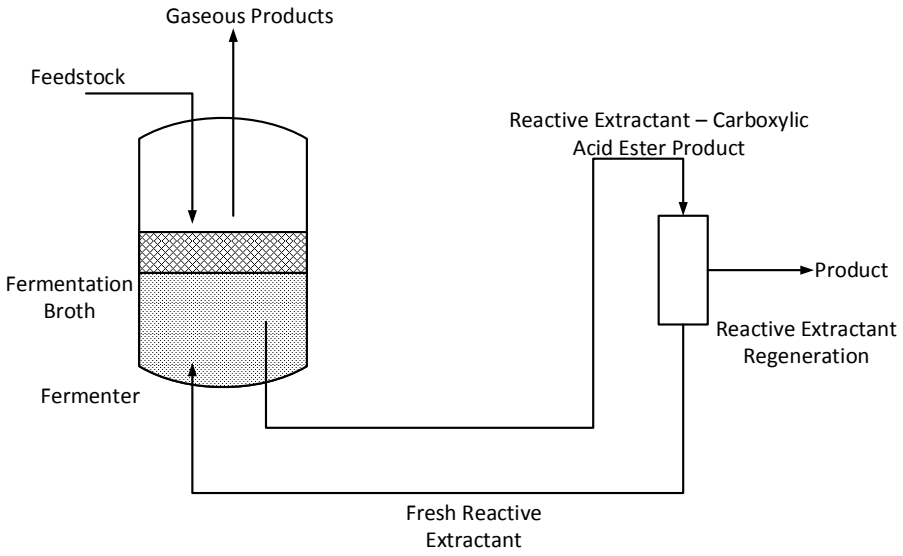

Figure 1. Simplified process scheme for the reactive extraction of carboxylic acids from fermentation broths.

To implement this idea, the development of reactive extractants with specific functional groups and their reaction with levulinic acid as an industrially relevant product model case, is currently underway. For an extraction process, equilibrium and kinetic data are important as this will help in the decision on the reactor/extractor system, e.g. if a non-agitated reactor can be used, or if fermentation and separation must be physically separated, employing a mixer-settler, a centrifugal or bubble column configuration. Physical and chemical properties of the extraction will be derived from equilibrium data. Kinetic data describing both, the mass transfer across the interphase, and the rates and orders of the reaction, are used to establish the reaction mechanism.

Conclusions

The extractant for reactive extraction can be designed based upon the solvent selection criteria. Utilization of solvents with functional groups could be a viable alternative for the recovery of different compounds present in low concentration from fermentation broths. This will render the

selective separation of the desired compound thereby improving process economics and overall production costs. The enhanced separation process will help to increase reactor productivity, thus facilitating the establishment of an efficient integrated biorefinery.

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