Process Modelling and Simulation for 1-Butanol Removing from Fermentation Broth by Extraction with Oleyl Alcohol

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Industrially 1-butanol is a petroleum-based chemical, which can be produced also using renewable biomass resources. 1-Butanol is used as a raw material for the production of bio-based alternatives to many petroleum chemicals, to fossil fuels additivation or, as an alternative fuel. It has higher energy content and lower vapour pressure in the same thermodynamic conditions if compared to methanol and ethanol and also exhibits higher miscibility with diesel fuel and gasoline. These characteristics make 1-butanol a better fuel than lower aliphatic alcohols. In the early 20th century, the fermentation of sugars by Clostridium acetobutylicum was used extensively for the industrial production of a mixture of 1-butanol, acetone, and ethanol. However, high substrate, fermentation and separation costs combined with low yields resulted in the demise of the fermentation process in favour of petrochemical production routes. Due to the present increased interest in finding renewable bio energy resource, recent research efforts have included genetic engineering to increase 1-butanol production, optimizing fermentation and reactor conditions. In the same time, efforts are made in order to find proper techniques for 1-butanol separation and purification. Among the solvents subject to be used in the separation by extraction, oleyl alcohol proved to be one of the most efficient. This alcohol has a rather high cost price but fulfils all the other requirements for a solvent (environment friendly, fire or explosion safe, easily to regenerate and reuse). If the solvent losses during operation are minimized it is possible that the separation process becomes profitable. The present paper presents the results obtained in modelling and simulation of a process unit for 1-butanol separation from the bio fermentation reactor product mixture using oleyl alcohol extraction, results that underlie the economic performance analysis.

Keywords: liquid-liquid extraction, 1-butanol, ABE fermentation, oleyl alcohol

1-Butanol is an important solvent and a potentially alternative biofuel. The alternative fuel 1-butanol can be produced via acetone-butanol-ethanol (ABE) fermentation (by Clostridium acetobutylicum) from renewable resources, i.e. biomass. ABE fermentation traditional technology suffers from a number of limitations as compared to ethanol fermentation. The fermentation is inhibited by the end products, especially 1-butanol, has a low product concentration, in addition to a high cost of product recovery [1]. Mixture produced by ABE fermentation contains up to 2-3% (by volume) alcohol, while the alcoholic fermentation of ethanol reaches 12-13% alcohol.

Expensive feedstock and the high costs for the separation of ABE from the dilute fermentation broth in the downstream processing have so far prohibited the industrial-scale production of bio-butanol.

To avoid the mentioned limitations, some attempts have been made to apply molecular engineering knowledge, genetic modification techniques used to force the evolution of microorganisms in order to produce a crop with improved characteristics in terms of production of alcohols (transformation yield in the fermentation product per unit mass of substrate). Some improvement has been observed in the mentioned decrease related to inhibition but an unwanted change in the ratio between the amount of components of fermentation products occurs also.

Other attempts to improve the fermentation consist in trying to use mutants of solventogenic genes and other microbes, such as E. coli in order to act effectively on the limitations described above. Tests are still under way.

On the other hand, the low productivity and 1-butanol yields of ABE batch fermentation can be increased by using a continuous fermentation with cell recycle and integrated product removal [2-4]. Since the fermentation product is consisting of three liquid phases (1-butanol is partially miscible with water), the separation by distillation is more complex and costly. Various configurations of distillation sequences for the separation of components contained in the effluent of an ABE fermentation process contain between 5 and 8 separation columns. In these sequences the separation consume about 12 tons of steam to purify a ton of ABE products, while ethanolic fuel distillation requires about 2 tons of steam consumption per ton of ethanol produced.

In situ solvent extraction during fermentation, which allows the continuous removal of 1-butanol from the bioreactor, has been shown to be one technique that enhances solvent production in ABE fermentation by reducing end product inhibition [5]. Removal of 1-butanol (or all of ABE fermentation products) from the fermentation mass by liquid - liquid extraction is considered an important alternative technique. Usually, the product of fermentation is mixed in an extractant insoluble in water extractant. 1-Butanol is more soluble in the mentioned extractant than the aqueous phase (fermentation broth), therefore a selective 1-butanol concentration in the extractant is produced. Since the extractant and aqueous media are immiscible, the extractant mass can be easily separated from the fermentation system after 1-butanol extraction. It should be noted that the liquid - liquid extraction process, above described, is able to extract the products of
fermentation reaction without removing the substrates, water or/and the useful nutrients.

A number of solvents have been experimentally studied and reported in literature, on the basis of 1-butanol selectivity, partition coefficient, their toxicity and biocompatibility. These solvents include oleyl alcohol, polypropylene glycol, olive oil, 2-ethyl-1,3-hexanal [7, 10], benzyl benzoate, dibuthyl phthalate [8] methylate crude palm oil [5] and 2 ethyl-1-hexanol [9].

This work reported the removal of 1-butanol from an acetone-1-butanol-ethanol fermentation broth by using the solvent extraction technique. The process was modelled and simulated using Aspen Hysys 7.1® process simulator. Operating conditions for 1-butanol separation as well as specific consumption of extractant and utilities were studied. Oleyl alcohol was used as extractant as being non toxic for the microorganisms.

**Process Modeling**

Modeling procedure was performed by using the representation of unit operations for the separation process by unit operation models already built in the commercial chemical processes simulator. NRTL LLE and UNIQUAC VLE models were used as properties packages. The vapour phase was modeled using the ideal gas assumption. Figure 1 presents the conceptual scheme of the process.

![Block diagram of the 1-butanol removing process](image1)

**Results and discussions**

A study on the effect of the volume ratio of fermentation broth to solvent at the ratio ranges between 1:1 and 1:2 showed that, when the ratio increased, the 1-butanol productivity increased. The best ratio for the separation system was 1:1.55 with a maximum concentration of 14.53 g 1-butanol/L. Temperatures range in the liquid-liquid extraction column was between 30 to 60°C. Changing the operating temperature from 30 to 60°C slightly affected the partition coefficient and extraction capacity of 1-butanol, but when the extraction temperature increased, the extraction capacity of acetone and ethanol easily increased. The best temperature for operating the extraction column was identified in the range of 45 to 50°C. Nevertheless, we have to consider the optimum temperature used in the mesophilic bioreactor which temperature should not be higher than 35°C [9].

In table 2 the main process streams characteristics are presented as resulted from the convergent simulation with temperature of 35°C in the extraction column.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>THE MAIN PROCESS STREAMS CHARACTERISTICS</th>
</tr>
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<tbody>
<tr>
<td>Component</td>
<td>kg/h</td>
</tr>
<tr>
<td>Water</td>
<td>8800.00</td>
</tr>
<tr>
<td>1-butanol</td>
<td>600.00</td>
</tr>
<tr>
<td>Ethanol</td>
<td>400.00</td>
</tr>
<tr>
<td>Acetone</td>
<td>200.00</td>
</tr>
</tbody>
</table>

In this paper modeling and simulation of liquid-liquid extraction and the separation of 1-butanol and solvent recovery processes was performed. Feed stream characteristics are given in table 1 and in figure 2 is presented the process topology given as process flow diagram, by the simulator.

![Process flow diagram for 1-butanol removing from fermentation system](image2)
Theoretically, the specific consumption of fresh extractant (obtained from the process simulation) was very low. Power consumption was of 15 kW per ton of separated products from ABE fermentation. Hot and cold utility consumptions per ton of separated products from ABE fermentation was of 2.6 MW and 2.8 MW respectively.

Conclusions
Separation of 1-butanol from fermentation mixture by liquid-liquid extraction is a valuable alternative compared to separation by distillation.

The modelled process maintains in the extraction column operating conditions favourable for the microorganisms involved in the fermentation and thus, 1-butanol separation using this process will avoid auto-inhibiting conditions for the fermentation process (by the continuous removal of 1-butanol), leading to a high economic efficiency both for the biochemical reaction unit as for the separation unit.

Despite the fact that oleyl alcohol is a fairly expensive material, operating costs are not influenced by its use because it’s specific consumption is insignificant. Only the value of the investment can be influenced by using this agent of selective extraction for 1-butanol.

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References

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