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BIOBUTANOL - PRODUCTION AND PURIFICATION METHODS

BIOBUTANOL - METODY WYTWARZANIA I OCZYSZCZANIA

Abstract: The prospective of depletion of natural resources, petroleum products and rising prices of raw materials tend to look for fuels from renewable energy sources and biofuels. The focus so far has been put on bioethanol due to the availability of raw materials for its production and well-developed methods for isolation and purification. Butyl alcohol - biobutanol can be regarded as a potential biofuel. Biobutanol is a very attractive energy source because - as opposed to bioethanol - is non-hygroscopic, does not cause corrosion and has a higher calorific value. Production of butanol may be made by a fermentation process called ABE (*acetone*, *butanol*, *ethanol*), carried out mostly by bacteria *Clostridium acetobutylicum*. The basic problem of wider use of biobutanol depends on its production with sufficient efficiency and this in turn is limited by separation of butanol from fermentation broth. The distillation process is not applicable. The classical extraction requires the use of a flammable or toxic liquid. For separation and purification of biobutanol it is proposed to apply ionic liquids. Use of ionic liquids for the extraction of butanol (to remove from the fermentation environment) can be achieved either through direct application of the liquid in the bioreactor and separation of butanol outside of bioreactor or directing fermentation broth outside the bioreactor and separation of butanol in the membrane contractor.

Keywords: biobutanol, renewable energy sources, ionic liquids

Production of butanol by the anaerobic fermentation is one of the oldest industrial method for obtaining this organic solvent [1]. In the early 20th century interest in butanol resulted from an inadequate level of supply of natural rubber and increase of its market price. At that time, butanol was used as one of raw material for the production of butadiene being a raw material for synthetic rubber production. Currently, butanol is considered as an alternative biofuel.

Butanol is a colourless, flammable alcohol. It is widely used in industry, among others, applied as a solvent. It arouses particular interest due to the role it can play in the future as a biofuel. It is expected that production biobutanol can reduce consumption of oil and natural gas by the automobile industry and reduce emissions of harmful gases into the atmosphere [2, 3].

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The petrochemical industry uses alcohols, mainly ethanol as a fuel additive, improving its quality. Research results show that the use of butanol for this purpose is much more useful than the application of ethanol. Butanol has a high calorific value, which is 29.2 MJ/dm^3 (melting point –89.5°C, boiling point 117.2°C, flash point 36ºC, the self-ignition 340ºC). Furthermore, it also has a relatively low heat of vaporization, and is less corrosive than ethanol. All these features enhance its usefulness both as an additive to gasoline, as well as biofuels. Currently, butanol is used only as an additive to gasoline because there is no engine working exclusively on this alcohol. However, intensive research is carried out in this direction. [2-4]. Table 1 gives the basic properties of butanol as a fuel in comparison with the other liquid biofuels.

Table 1

Properties of butanol and other biofuels [5]

Fuel	Combustion energy [MJ/dm^3]	Evaporation heat [MJ/kg]	RON Research Octane Number	MON Motor Octane Number
Petrol	32	0.36	91÷99	81÷89
Butanol	29.2	0.43	96	78
Ethanol	19.6	0.92	130	96
Methanol	16	1.2	136	104

The process of biobutanol production

Butanol can be obtained using several chemical technologies. It is also possible to produce butanol in the process of fermentation by means of bacteria of the genus *Clostridium*. This process occurs under anaerobic conditions, and butanol as one of the products - called biobutanol [2, 6].

The most popular bacteria species used for fermentation is *Clostridium acetobutylicum*. Such fermentation is so called ABE (*acetone-butanol-ethanol*), due to the names of the main products of this process, the typical ratio of these compounds being 3:6:1. The final concentration of butanol is about 3% [2, 7].

In the course of industrial production of biobutanol, using a fermentation process one must take into account three factors, evaluation of the process profitability: the cost of raw material and its pretreatment, a relatively small amount of product obtained, its significant toxicity, cost of product recovery from fermentation broth. *Clostridium acetobutylicum* belongs to the amylolytic bacteria; therefore a good substrate for production of butanol for these bacteria is starch. Nevertheless, the use for the fermentation crop products is not very economical; primarily because of too high price due to demand for these products from food industries. Therefore, for the production of butanol there are commonly used agricultural wastes for example: straw, leaves, grass, spoiled grain and fruits etc which are much more profitable from an economic point of view. One looks for other sources of plant biomass, which production does not require a lot of work and costs (eg algae culture) [2, 8, 9].

Modern research on the production process of biobutanol focuses on finding the best kind of substrate for fermentation process and for efficient strain of bacteria. Potentially, one can use all the waste containing monosaccharide, and polysaccharides and waste glycerol. Analogously, the biomass of algae is one example of such a substrate. Algae culture does not require intensive labour and high costs. Some of the micro-algae contain relatively high percentage of sugars in dry matter, such as *Chlorella* contains about 30÷40% of sugars, which greatly increases their usefulness in the production of biobutanol.

There is also carried out research on the genetic modification the bacteria *Clostridium acetobutylicum* and *Clostridium beijerinckii* in order to increase the resistance of bacteria to the concentration of butanol in the fermentation broth.

Methods for removal of butanol from the broth

The method eliminates the toxic effect of butanol on bacterial cells is a systematic removal of this compound from the fermentation broth. The traditional method of product recovery is distillation. As butanol has a higher boiling point than water, therefore, this process consumes much energy, and therefore it increases the cost of the whole process, especially at low concentration of butanol in the broth. Distillation is a process energetically and economically unfeasible, as the boiling point of water is lower than the maximum concentration of butanol and butanol fermentation broth is 3% by weight. This leads to low productivity and high costs of separation and purification of butanol [10, 11]. Therefore, currently other methods are used such as adsorption, membrane pertraction, extraction, pervaporation, reverse osmosis or "gas stripping" [12]. Particularly, much attention is paid to the method of pervaporation, which is potentially promising way to recover butanol from fermentation broth, as it allows separation and concentration of the product during a single process.

Butanol recovery by adsorption

Adsorption is investigated in the butanol separation from fermentation broth but the capacity of adsorbent is very low and cannot be used on industrial or semi - industrial plant. A variety of materials can be used as adsorbents for butanol recovery, but silicalite is the one used most often. Silicalite, a form of silica with a zeolite-like structure and hydrophobic properties, can selectively adsorb small organic molecule like C1–C5 alcohols from dilute aqueous solutions. Removal of butanol from fermentation broth by adsorption from the liquid phase can be used only in laboratory scale. This follows from the small-capacity of adsorbents for butanol. For this reason, the separation process is not suitable on an industrial or semi-technical scale.

Butanol recovery by membrane reactor

One of options of butanol removal is to use methods of immobilization of microorganisms in the membrane or the use of membrane reactors. For example, in the capillary membranes (hollow fiber) the increase in efficiency from 0.39 $g/dm^3/h$ to 15.8 $g/dm^3/h$ was attained. On industrial scale cell immobilized technique gives more disadvantages like poor mechanical strength and increase mass transfer resistance. Also, leakage of cells from the matrices is a frequent problem.

Butanol recovery by gas stripping

Among various recovery techniques, gas stripping is a promising technique that can be applied to butanol recovery during ABE fermentation [7, 13, 14]. Separation of volatile compounds can be obtained by lowering the pressure, heat or the use of inert gas. In many practical applications, a combination of these techniques is applied. By introducing the solution into the column in countercurrent to the gas (inert) one achieves the separation of specific components. In this case they are butanol, ethanol and acetone.

Butanol recovery by pervaporation

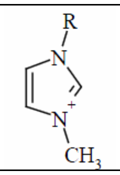
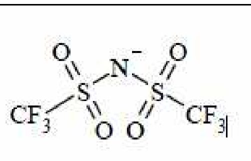
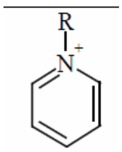
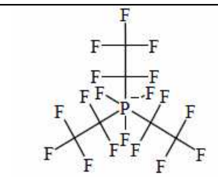
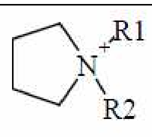
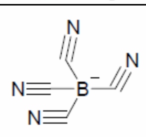
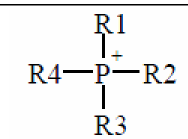
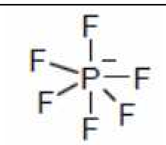
Pervaporation is one of the promising techniques for the removal of toxic substances for *Clostridium acetobutylicum* such as butanol, ethanol and acetone. This method involves the selective transport by diffusion of some components thrugh a membrane. A vacuum applied to the side of permeate. The permeated vapours should be condensed on low pressure side. Membrane in this case ought to be a hydrophobic polymer since transportation of organic components from the fermentation broth is preferred. Polydimethylsiloxane membranes and silicon rubber sheets are generally used for the pervaporation process. The drawback of the method can be high costs to produce low pressure at low pressure side of the membrane. Selection of a suitable polymer forming the active part of the membrane is a crucial issue in this case.

Application of ionic liquids

Release of butanol from fermentation broth is a very difficult technical problem. The extraction process using conventional solvents may be useful, but requires the use of solvents which are often volatile, toxic and dangerous.

Table 2

List of cations and ions in ionic liquids, IL

Cation	Anion
	
	
	
	

In recent years one may observe a growing interest in ionic liquids, IL as non-volatile, environmentally friendly solvents for various chemical processes. Ionic liquids can provide a solution in the case of butanol extraction from fermentation broth. Ionic liquids are organic salts present in the liquid state at room conditions, have very low vapour pressure and low solubility in water. Hence, IL is valuable solvent in the extraction process from aqueous solutions [15].

The following combinations of cations and anions constituting the IL are shown in Table 2. They are promising, due to the properties as a liquid extraction, in the system water - butanol - IL.

Combinations of cations and anions give 16 different IL. In addition, the substitution of the corresponding radical in the structure of cations allows obtaining several times more IL that can be taken into account in designing a suitable ionic liquid to test the extraction process. Studies on the properties of ionic liquids and in particular their possible extraction is currently undertaken and the results of experiments are reported in the literature [15-17].

The use of ionic liquids for the extraction of butanol (to remove from the environment fermentation) can be realized through direct application of the liquid in the bioreactor, and the separation of butanol outside the bioreactor. The diagram of such a solution is shown in Figure 1. Fermentation broth with the addition of the ionic liquid is introduced into the bioreactor. Selected IL should be verified if it is not toxic to the bacterium *Clostridium acetobutylicum*. As a result of contact of the IL with broth the extraction of biobutanol take place simultaneously with other metabolic products such as ethanol and acetone.

Due to the extremely low solubility of IL in water the fraction of the extract constitutes a separate phase, which must be derived from the environment of bioconversion and enter evaporator where the ingredients are extracted and will be distilled. Regenerated ionic liquid after a suitable cooling is recycled to the fermentation tank. Removal of bioconversion products makes further progress towards the transformation of raw materials into biobutanol.

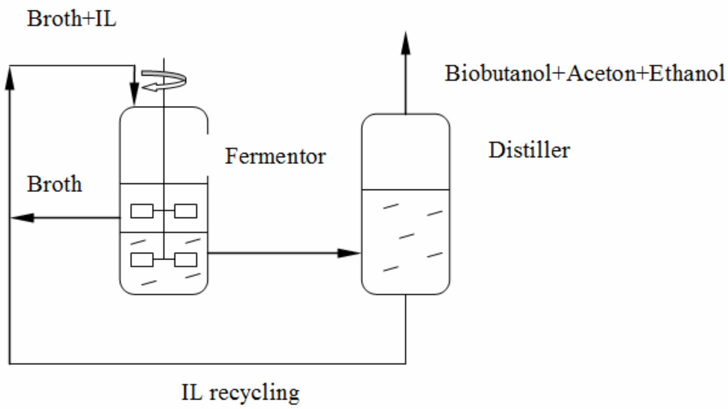


Fig. 1. Application of the IL *in situ* in the bioreactor

Another option is the use of ionic liquids removal of fermentation broth outside the bioreactor and the separation of butanol in the membrane contractor.

Conclusions

1. Biochemical method for obtaining biobutanol is more efficient and less costly in comparison with the methods of chemical synthesis. The basic problem that arises in the application of biochemical methods is a low concentration of biobutanol fermentation broth resulting from the toxic properties of the metabolic products of the bacteria *Clostridium acetobutylicum*
2. The metabolic engineering of different than *Clostridium* bacteria for butanol production is probably the most promising strategy for butanol biosynthesis [18].
3. A promising method of biobutanol separation from the fermentation broth is the use of ionic liquids. The following options are promising for their practical application: the use of IL *in situ*, or extraction with the application of membrane contractors.
4. Use the biobutanol in industry causes a positive ecological effect. Biobutanol as a fuel additive is a better component for hydrocarbon fuels in relation to other alcohols. Its application would result in reductions of greenhouse gas emissions.

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BIOBUTANOL - METODY WYTWARZANIA I OCZYSZCZANIA

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Abstrakt: Perspektywa wyczerpania naturalnych zasobów produktów ropopochodnych oraz rosnące ceny tych surowców skłaniają do poszukiwania paliw z odnawialnych źródeł energii, czyli biopaliw. Główna uwaga do tej pory skupiona była na bioetanolu ze względu na dostępność surowców do jego wytwarzania i dobrze opracowane metody wydzielania i oczyszczania. Alkohol butylowy (biobutanol) może być traktowany jako potencjalne biopaliwo. Biobutanol jest bardzo atrakcyjnym źródłem energii, gdyż - w przeciwieństwie do bioetanolu - jest niehigroskopijny, nie powoduje korozji i ma większą wartość opalową. Produkcja butanolu może odbywać się w procesie fermentacji zwanej ABE (*aceton*, *butanol*, *etanol*), przeprowadzanej najczęściej przez bakterie *Clostridium acetobutylicum.* Podstawowy problem szerszego wykorzystania biobutanolu leży w jego wytwarzaniu z odpowiednią wydajnością, a ta z kolei jest limitowana wydzielaniem butanolu z brzeczki fermentacyjnej. Proces destylacji nie jest w tym przypadku możliwy do realizacji. Klasyczna ekstrakcja wymaga zastosowania cieczy albo palnych, albo toksycznych. W celu wydzielania i oczyszczania biobutanolu proponuje się zastosowanie cieczy jonowych IL. Wykorzystanie cieczy jonowych do ekstrakcji butanolu (usuwania ze środowiska fermentacji) może być zrealizowane albo poprzez bezpośrednie zastosowanie cieczy w bioreaktorze i oddzielenie butanolu na zewnątrz bioreaktora, albo poprzez wyprowadzenie brzeczki fermentacyjnej na zewnątrz bioreaktora i oddzielanie butanolu w kontraktorze membranowym.

Słowa kluczowe: biobutanol, odnawialne źródło energii, ciecze jonowe