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METHODS OF LIQUID BIOFUEL PRODUCTION - THE BIODIESEL EXAMPLE

Abstract: The main problem for present fuel producers is how to cover the demand for new, alternative fuels (biofuels) as a substitute or components of traditional fuels. In this purpose the technologies of biofuels production are still being improved. To show how wide the area of research in this field is, authors of this paper have compared various types of biofuel production methods, pointing out the raw materials needed for their synthesis. Conversion processes, which are used to alternative fuel’s production, were also presented. Further in this article authors focus on the more detailed statement and description of today’s most popular biodiesel technologies, along with the details of selected parameters and efficiency of installations based on those technologies. This work is a gathering of current knowledge on FAME technology production.

Keywords: biofuels, biodiesel, technology of production

Introduction

The demand for renewable energy sources and alternative fuels is constantly growing. This is a serious argument for potential producers to invest and develops new, more efficient technologies for biofuels production, especially because of the limited amount of fossil fuel.

Liquid biofuels belong to the few groups of compounds with properties and parameters which allow their use in relevant types of internal combustion engines. The main types of biofuels are bioethanol and biodiesel, and their blends with fuels, like bioethanol with gasoline and biodiesel with diesel fuel. Sometimes there could be found a mixture of diesel fuel with ethanol, the oxydiesel or bioxydiesel type [1].

The main types of liquid biofuels and biocomponents are [2, 3]:

- bioethanol - anhydrous ethyl alcohol produced from biomass or biodegradable waste from fermentation or dehydration process;
- bioesters - methyl esters produced from vegetable oils or animals fats;
- biomethanol - methyl alcohol (CH₃OH), produced from biomass. Biomethanol can be obtained by dry distillation of wood or the Fisher-Tropsch reaction of the gas obtained by gasification of biomass. Unfortunately methanol is toxic and its production process is expensive. In Poland Prof. D. Nazimek from UMCS works on catalytic synthesis of methanol from CO₂ and water, which may hopefully decrease the costs [4, 5];
- bio-ETBE (Ethyl tert-butyl ether) - produced on the basis of bioethanol. Synthesized by isobutylene (from petroleum) and ethanol (from fermentation process) mixing.

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Bio-ETBE is used as a biocomponent in fuels, in accordance with EN 228 standard (up to 15% v/v);

- **bio-MTBE** (Methyl tetr-butyl ether) - produced on the basis of biomethanol. Obtained in the distillation of wood or isobutylene with methanol reaction. Bio-MTBE is used as a gasoline biocomponent, but its parameters are worse than bio-ETBE. Due to this fact and the greater toxicity of the product justifies much less production of bio-MTBE than bio-ETBE;

- **bio-DME** - Dimethyl ether ($\text{CH}_3\text{OCH}_3$) produced from biomass. It is gaseous fuel for diesel engines, characterized by high cetane number (over 55). It can be obtained from synthesis gas (gain from biomass gasification), or from dehydration of methanol. Unfortunately, the use of this fuel is associated with various problems including fuel injection, and so far it is not commonly used as fuel;

- **pure vegetable oils (PVO)** - which are oils produced in fat processing plants by cold pressing and extraction, as crude oil or refined but not chemically modified;

- **biobutanol** - produce from biomass and biodegradable waste. It is a mixture of isomeric alcohols like: $\text{n-butanol}$ (1-butanol), sec $\text{butanol}$ (2-butanol), isobutanol (2-methyl-1-propanol), tert $\text{butanol}$ (2-methyl-2-propanol). Butanol can be obtained by chemical reactions or using biotechnology. In fermentation process bacteria like $\text{ie}$ *Clostridium Acetobutylicum* can be used. This bacterium has the ability to produce butanol from sugar beets, sugarcane, wheat, corn, straw or wood waste. Biobutanol is similar fuel to gasoline (calorific value: butanol - 29 MJ/g, gasoline - 32 MJ/g) and is used in an amount of 8-32% as a gasoline component to increase its octane number.

**Industrial methods of transesterification process**

Production of biodiesel can be carried out both periodically and continuously. First type approach prevails mostly in small installations, working for one or several groups of farmers. The amount of biodiesel obtained this way is usually less than 20 thousand tons per year, and a single periodic cycle takes from 6 to 24 hours [6]. In order to achieve an adequate mixing of the substrates special reactors with mechanical mixers (axial propeller) are being used in the process. They are filled with vegetable oil and an appropriate amount of catalyst mixture consisting of methanol and a catalyst. Then, for about 1 hour, the reaction mixture is mixing. The solution proposed here is applied by many companies which provide FAME (*fatty acid methyl ester*) installations. The Polish companies are: Promar from Poznan [7], IMIX Biofuel [8], Bio-Tech [9], Hydrapres et al [10]. There are also methods for mixing the raw materials with combined techniques. The company Protechnics [11] *ie* has in its offer installation using the mixing in the pipe, combined with additional mixing by a pump.

*Biodiesel production method used by the Henkel company*

The main difference between available in the market large biodiesel plants, rely mainly on different techniques of mixing oil with methanol and catalyst. For example Henkel offers a number of static mixers containing special design pads, which cause turbulence flow and intensify mixing.
Fatty acids (vegetable oils) after heating in heat exchanger and mixing with catalyst and methanol, go to flow tubular reactor, in which the reaction mixture is still intensely mixed. Products are decanted in a separator. Esters fraction with unreacted oil goes to the second part of the process. After that glycerine fraction goes to separator. This process goes in two stages, but if it is necessary they could be repeated.

**Biodiesel production process used by Lurgi company**

The continuous process developed by Lurgi company provides another type of installation. The reaction has two stages but in contrast to previous solution, the mixing process is done by using mechanical stirrers placed directly in transesterification reactor. After that, the reaction mixture goes to separator and subsequently is pumped to second reactor. Products, after second stage of the process (mixture of FAME, glycerine and methanol), are re-routed to separator. Unreacted oil (after separation) is returned to first stage of process. Glycerine, methanol and esters of rapeseed oil are neutralized by phosphoric acid in mixer and then goes to centrifuge. In distillation column glycerine and methanol are separated and then recycled to process. Separated in centrifuge water is stored in tanks. From the washing water could be recovered potassium-phosphorus fertilizer, which the main compound is $K_2PO_4$.

**Multistage technology by Connemann**

It is also known as CD technology (*continuous deglyceration*), and was developed and patented in 1990 (DE 4209779, US 5,354,878). In 1996 the worldwide production of biodiesel in this technology reached level of 120 000 Mg [12], and the product meets the high requirements (standard DIN EN 14214). Currently production decreased to the one company in Czechowice-Dziedzice [13].

Transesterification process is similar to previous technologies, but by multistage glycerin draining and methanol-catalyst addition, higher yield and purity of the products can be obtained [14]. From 1015 kgs of oil and 109 kgs of methanol they could produce 1000 kg of high quality biodiesel, with the cetane number about 54-58, and only 96 kg of glycerine (99.7% purity) [12].

**Esterification of soybean oil technology**

The kinetics of transesterification reaction of soybean oil with methanol and NaOH, studied by Noureddini and Zhn [15], results in developing new technology [16].

In this technology substrates are brought through the feeder serially connected to the static mixers with inserts, which provides turbulent flow. Second mixer has got water jacket to allow temperature control of the reaction mixture, which is directed from it into the reactor with a mechanical stirrer. Esterification reaction is then carried out in the tubular flow reactor. So, the reaction starts in the mixer, but continues and ends in tubular flow reactor. Biodiesel and glycerin products after cooling in a heat exchanger can be separated in the disc separator or as described in [14] and [6] in gravitational separator.
Esterification of used fats by LUT Technology

The technological process of LUT (Lappeenranta University of Technology) [17] was developed for waste oils (vegetable oils - mainly palm oil, and animal fats with high FFA (free fatty acids)) into biodiesel processing. In the first stage of process waste fats with FFA are esterificated in the reactor. Then the substrates are directed to subsequent reactors, in which vegetable oils, methanol and H₂SO₄ (as a catalyst) are being mixed, and two stages transesterification occurs. Glycerin from ester and unreacted fatty acids separators, together with glycerin from biodiesel separators have been placed between the reactors.

In the glycerine fraction methanol, sulphuric(VI) acid and water are diluted. This mixture is heated in heat exchanger and separated by distillation under reduced pressure. Products of distillation are: pure technical glycerine, methanol and water. Methanol could be return into process.

ICHP technology

ICHP is one of the first technology developed by the Institute of Industrial Chemistry (ICHP) in Warszawa. Nowadays, after new technology was described and patented [18], [19], this name of process has only historical meaning. In this process a catalyst is a sulphuric acid (H₂SO₄). Methanol vapours, overheated in superheater, are directed to vertical, tubular reactor. Stream of compounds goes into reactor from the bottom and with countercurrent to oil. Bubbles are floating upwards causing pneumatic mixing of the components. Two stages of process: esterification and transesterification takes place between 90-120°C. In separator the glycerine fraction is isolated from FAME. Unreacted methanol vapours with water are condensated in the condenser and rectified in rectifying column. Methanol is compressed, overheating and then is returned into reactor [6].

Cvengros-Powazanec method

In this process (proposed by Slovak researchers J. Cvengros and F. Powazanec) seeds are pressed without heating with the efficiency of about 83%. From one ton of seeds approximately 340 kg of oil could be produced. Pressing is carried out in low capacity oil presses at temperatures below 70°C. Two stages transesterification process takes place in 1.3 m³ reactor at temperature level between 60-70°C, with NaOH (3-6%) as a catalyst. In first stage of process the oil-to-methanol molar ratio is 1 : 3.5, in second 1 : 0.95. After the reaction, residue of methanol is being removed by blowing air and products separated from glycerine phase. Esters are neutralized with phosphoric acid, and free fatty acids with ammonium hydroxide. Soap, free fatty acids and methanol (by adding phosphoric acid) are also being removed from the glycerin phase. After such purification crude glycerin is obtained [20].

Vogel & Noot process

This Austrian company produce methyl esters under the commercial name of “BIO diesel”. Installation works in two-stage semi-continuous system, and the catalyst is a 2% potassium hydroxide, which is added as a mixture with methanol. The recovery of methanol is carried out with two phases. Glycerine phases from both stages are being mixed. The
phosphoric acid is added in order to separate the free fatty acids and neutralize the excess of KOH. Free fatty acids may be collected as a separate product or returned back to the esterification process. Crude glycerine could be sale or purified. The potassium phosphate, formed from the remnants of the catalyst and phosphoric acid, is used as a component of mineral fertilizers.

Other technologies of FAME production

The IKA POL company has an interesting way of biodiesel production process conducting, which uses ultrasonic reactor. The preheated oil with the catalyst mixture and methanol is transported through a pipeline into the flow cell. The esterification reaction runs there with the help of ultrasonic waves, which cause mixing intensification.

Then in the centrifugal separators the post-reaction mixture is separated to FAME and glycerine. Residence time of the reactants in the installation in this continuous technology takes only about 20 min, the reaction lasts for 5 min, and the time of separation is less than 15 min [14, 21].

The new technology of biodiesel production is used in the systems, which are offered by the Uni-Masz company. Single installation is running in a continuous process, and has a capacity of 1.5 m$^3$/h. Substrates mixing and transesterification reaction is carried out through a mixing pump, with an additional microwave radiation exposure. Further process including gravitational separation of the products is conducted in a flow tank. Improved quality of produced FAME is obtained by washing esters with liquid extractant derived from vegetable oil processing. The use of microwaves allows better mixing of raw materials and faster separation of the products [22].

Summary

The main technologies of biodiesel production are described in this study. Of course they are not the only possibilities of obtaining alternative energy source. Certainly they are not all the options, furthermore demand for new, cheaper and more efficient technology is way of determines new invention [23]. The collection of these technologies, however, allows a large extent on the systematization of knowledge on this subject and is a good starting point for further analysis in the field of biofuels.

References

METODY PRODUKCJI BIOPALIW CIEKŁYCH
NA PRZYKŁADZIE BIODIESLA

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Abstrakt: Zapewnienie pokrycia zapotrzebowania na nowe, alternatywne źródła energii, które można z powodzeniem wykorzystywać jako substytut bądź dodatek do paliw tradycyjnych, od jakiegoś czasu stanowi główny cel wielu firm zajmujących się ich produkcją. W tym celu opracowano i w dalszym ciągu udoskonala się coraz więcej technologii wytwarzania paliw zastępczych, zwanych biopaliwami. Aby wskazać, jak szeroki obszar obejmuje badania w tym zakresie, w niniejszej pracy porównano ze sobą różne rodzaje biopaliw, wskazując surowce potrzebne do ich produkcji oraz procesy konwersji prowadzące do uzyskania poszczególnych produktów. Mając na uwadze rozmiar zagadnienia, w dalszej części artykułu skupiono się na bardziej szczegółowym zestawieniu i opisie najpopularniejszych obecnie technologii produkcji biodiesla wraz z wyszczególnieniem wybranych parametrów pracy oraz wydajności instalacji opartych na tychże technologiach. Praca przybliża aktualny stan wiedzy z zakresu technologii produkcji FAME.

Słowa kluczowe: biopaliwa, biodiesel, technologie produkcji