New, innovative and sustainable transportation fuels

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1 Introduction

Secondary products from the industry – e.g. by-products of food and paper/pulp industry – can be used to manufacture new liquid biofuels or fuel components. A particularly interesting alternative is provided by butanol, which can be produced from biomass, since it seems to be most suitable for replacing petrol as fuel in gasoline engines. Besides, it is very energy efficient and also suitable to be produced on an industrial scale. Production of biobutanol and other higher alcohols is studied in the research project "New, innovative sustainable transportation fuels for mobile applications; from biocomponents to flexible liquid fuels (SusFuFlex)". The project is carried out as a joint project between the University of Oulu and Åbo Akademi University. It is financied by the Academy of Finland in 2008–2011, within the research programme for Sustainable Energy.

2 Objectives of the research

Research focuses on the production of higher bioalcohols and other compounds suitable as oxygenates (e.g. butanol, pentanol, mixed alcohols; e.g. glycerine ethers, glycerol carbonate). The objectives of the research are 1) to evaluate the old and novel procedures for microbiological production of butanol, higher alcohols and oxygenates as fossil fuel substitutes, 2) to develop and optimize catalytic materials and chemical reaction routes for the production of higher alcohols and other bio-derived compounds applicable as gasoline fuel and its additives, 3) to conduct a sustainability analysis of the processes to be developed, to analyze the atom economy of the new processes and to make a preliminary economical analysis, and 4) to integrate the processes and know-how developed by the research groups.

3 Microbiological approach in biobutanol production

3.1 Pre-treatment of biomass

The conversion of biomass to fermentable sugars before the fermentation is a challenging task, a reason why pre-treatment of biomass (wood-based cellulose or a low-value by-product from food industry) is required. Lignocellulosic materials (bark sludge, bio sludge and fiber sludge from a pulp mill) were dissolved in ionic liquid and the aim was to convert cellulose into sugars. The second aim was the successful fractionation of samples with liquid-liquid extrac-

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tion for chemical analysis. The real samples, if suitable for conversion of cellulose to sugars, could then be utilized in the biofuel production e.g. by fermentation.

Sample pre-treatment procedure was developed. Dried samples were characterized and dissolved in ionic liquid, 1-butyl-3-methylimidazolium chloride [BMIM][Cl]. This ionic liquid dissolved fiber sludge totally. Instead, the bio sludge did not dissolve at all and the bark sludge dissolved only partly. The samples were fractionated by liquid-liquid extraction and the fractions were analyzed by GC-MS, ESI-MS and HPLC. Based on the preliminary results, all samples showed the presence of cellulose, while glucose was found only in some of the samples. The fiber sludge seems to be the most potential biomass resource for further studies. (Holm et al., 2009)

3.2 Fermentation process

Microbiological approach starts from biomass by means of fermentation. Several *Clostridium* species are able to metabolize carbon compounds to butanol (butyric acid as an intermediate) in high yields (Biepl 2001). Biobutanol production is a two-stage fermentation process where acetic and butyric acid, CO_2 and H_2 are first produced in the acidogenic phase. Then the culture undergoes a metabolic shift to a solventogenic phase, and acids are converted to acetone and butanol. The product inhibits the yield of butanol and acids, making an integrated product separation process highly favourable.

Clostridial fermentation system was established including anaerobic reactor system (2 L) with temperature control and pH monitoring, cell immobilization unit, and fermentation medium circulation. Higher cell concentration and shorter lag phase prior to fermentation were achieved by cell immobilization. Without any further optimization, 2.1 g/L of butanol was produced from whey permeate supplemented with a yeast extract. Simultaneously, butyric acid was produced 5.8 g/L and acetic acid 3.2 g/L, suggesting that the acidogenic phase was working more efficiently compared to the solventogenic phase. Also the two-step fermentation, where acid products from *C. tyrobutyricum* fermentation were fed to the *C. acetobutylicum*, was tested. Fermentation system will be further developed and optimized, and experiments with whey and other substrates will be done. A product removal system will also be included into the fermentation system. (Päkkilä, 2008)

4 Chemical reaction routes

As a second approach, chemical reaction routes starting from compounds such as glycerol (a by-product of the 1st generation biodiesel manufacturing) or methanol/ethanol by means of novel catalytic processes is studied.

Synthesis of novel catalyst materials (nanostructured solid support materials) was performed. These materials are utilized as heterogeneous catalyst supports, but also supports for immobilized IL–enzyme fermentation catalysts. For such purposes, the research group is intending to implement (a) freestanding films of mesoporous oxides made by the anodization of corresponding metals, and (b) templated membranes of CVD-grown carbon nanotubes. Structural analyses

of catalysts and support materials are studied to investigate correlation between catalyst parameters (size, morphology) and catalyst performance (selectivity, efficiency). The fundamental reasons of catalyst deactivation are also studied. (Toukoniitty et al. 2009a)

A high throughput catalyst screening/testing reactor set up was developed for rapid preliminary testing of potential catalysts. The micro bomb reactors allowed simultaneous testing of 8 catalysts using only 10–50 mg of catalyst and 1.5 ml of ethanol. Reactors were equipped with magnetic stirring and typical testing conditions were 250°C and 80 bar. Microreactor results were validated (reproducibility, repeatability) and compared with the results obtained under controlled conditions (pressure, temperature) in a 300 ml Parr autoclave. Over 60 catalysts were tested for the direct catalytic conversion of ethanol to 1-butanol. Catalyst and support crystal structure was analyzed by XRD, catalyst particle size by XRD, size distribution by TEM and chemical composition by EDX. Preliminary testing of carbon nanotube and anodic aluminium oxide based heterogeneous catalysts was also performed. Mechanistic studies (300 ml Parr autoclave) were carried out to understand which factors influence the model reaction. Particularly, the effect of water removal, solvent and the catalyst pre-treatment (oxidation, reduction) were studied. (Toukoniitty et al. 2009b)

Further, the reaction of primary (methanol, ethanol) and secondary alcohol (glycerol) was studied over iridium catalysed reaction. The reaction conditions (pressure, temperature, molar ratios) were optimised. n-Butanol was produced in some reactions, but at its best the conversions of glycerol were low (<5 %) and selectivities were not high enough. A new pressurized microreactor system (10–15 bar, temperature up to 300°C) was developed. This enables the use of gaseous reactants as well. (Niinimaa, 2009)

Kinetic experiments were performed with the best catalyst (commercial HTC-500 Ni on alumina catalyst). Based on the results, the reaction of ethanol to 1-butanol is feasible under the studied conditions. Relatively high ethanol conversion and selectivity towards 1-butanol can be obtained by the employed one-pot approach in the presence of catalyst at elevated temperature (250°C). The mechanism of the reaction remains, nevertheless, still an open question. The obtained 30% ethanol conversion with 70% selectivity without optimization of reaction conditions and catalyst composition is a very promising result. The thermodynamic limitations exposed by the formed products can be overcome by optimizing reactor design and reaction conditions (e.g. temperature and pressure). Overall this reaction represents an excellent possibility to produce biofuel replacing modern gasoline. (Toukoniitty et al. 2009b)

5 Main challenges and opportunities

Research involves big challenges as well as several opportunities. The main challenges in the microbiological approach are 1) digestion of the raw material to fermentable sugars, 2) complex multistage fermentation process, 3) inhibition caused by the high solvent content, and 4) the decomposition of solvent and the loss in microbiological activity. The recent progress in butanol fermentation techniques (e.g., immobilization of microorganisms and separation of

acidogenesis and solventogenesis to different bioreactors) has partly solved these problems. Separation of butanol is also a technological challenge. It can be carried out without distillation due to the limited water solubility, since butanol forms a separate phase only after the concentration exceeds 7%.

The second approach, chemical conversion, is more challenging because a direct catalytic reaction route from glycerol involving e.g. chain elongation is currently not available in the literature. Therefore, entirely new synthesis routes and catalyst development is required. However, certain concepts adapted from recent literature are expected as key-steps for the desired goal. The integration of both the fermentation and the chemical route for chemicals suitable as liquid fuel substitutes or additives is also considered.

These technologies are expected to be applicable for the conversion of glycerol (a higher alcohol) and lower (bio)alcohols into high-value liquid fuels and fuel components. Especially, the successful use of industrial by-products in biobutanol production would open up new possibilities since butanol is a direct biofuel, and therefore it can be burned in the existing gasoline engines without any engine or car modifications. Butanol and pentanol have higher energy contents than ethanol, which is particularly important as the amount of biofuel in the fuel mixture increases. Compared to ethanol, biobutanol can be blended at higher concentrations with gasoline for the use in existing cars without the need to retrofit as the air-fuel ratio and energy content is closer to that of gasoline. Higher alcohols are also less water soluble and less corrosive than ethanol. Finally, one advantage of butanol is the fact that it can be distributed via the existing pipelines for gasoline and diesel.

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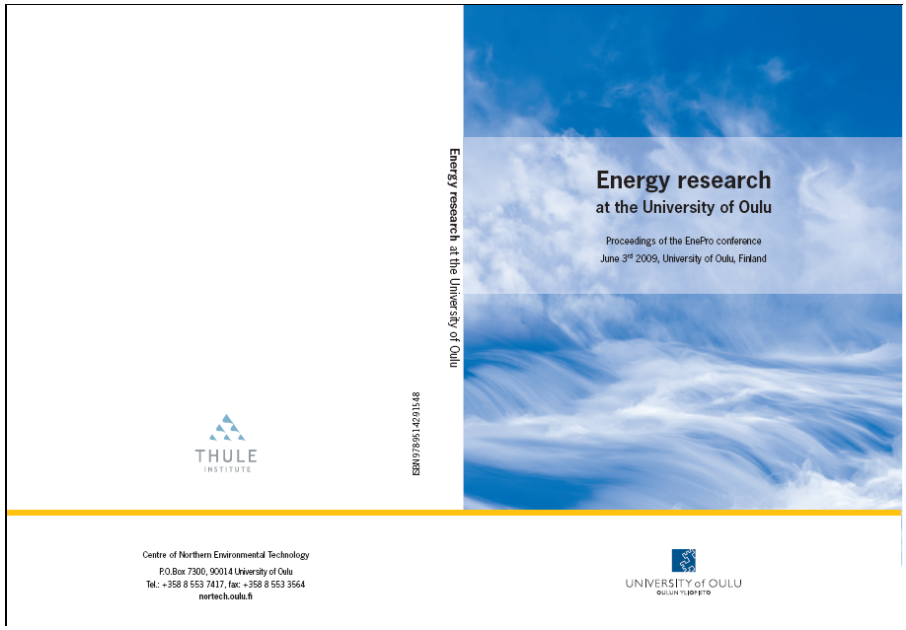

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