APPLICATION REPORT

High pressure reactor
Basic pathways for production of Bioethanol and Biodiesel

Biofuel
Simplification of established techniques for Biofuel production

The fields of application for Berghof highpreactor are chemical reactions proceeding at increased temperature and pressure demand with a maximum at 260 °C / 200 bar which can be found in various sectors of chemical engineering. Ideal reaction conditions are realized due to the modern and diverse design of highpreactor. In the present series of highpreactor Application Reports an overview on selected research topics is given. The intention is not to provide exhausted scientific information but an introduction to various topics for our customers. All application reports are based on scientific articles published mainly by Berghof highpreactor users. Original literature is cited at the end for further reading.

Introduction

In recent years the high energy demand of industrialized countries, energy security politics due to the growing fossil-based greenhouse emission, and the strong dependency on fossil fuels evoke an increasing awareness of the utilization of alternative sources of petroleum-based fuels derived from biomass. Biofuels comprise a wide number of fuels namely solid biomass, liquid fuels and biogas derived from organic feedstock.

For instance, the directive 2009/28/EC of the European Parliament and of the Council on the promotion of the use of energy from renewable sources controls and regulates the usage of biofuels in Europe. With respect to sustainability till 2020 member states are requested to reach a certain target for energy from renewable sources in transport (for detailed information see DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23. April 2009).

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With effect from 2017 the greenhouse emission saving from using biomass-based fuels shall be 50 % and in the following years at least 60 %. The raw material used for the production of biofuels is subject to the sustainability criteria for biofuels and bioliquids with strict norms considering nature and environmental protection, respectively.

Moreover, the global oil demand and energy usage is constantly growing. It was estimated by the International Energy Agency (IEA) that the global oil demand in 2010 grew to 86.5 million barrels a day (formerly 170.000 barrels a day) caused by the economic growth of developing countries. Hereby, the transportation sector shows, with around 55 %, the highest worldwide oil consumption rate. Altogether, the worldwide annual energy consumption in 2008 was 435 quadrillion BTU. Whereby, oil (33 %) is the most important energy source in the world, followed by coal with 27 % of the total energy use.

The use of renewable energy sources is constantly growing. In 2008, 19 % of the world energy consumption was supplied by renewable sources. With respect to sustainability in the near future more effort will be put in the energy sector using renewable energy sources. Biofuel from renewable feedstock are a hot topic caused by the fact that transportation accounts for 20 % of the global energy use.

Commonly, different generations of biofuels are distinguished. For first generation biofuels, just a small part of crops can be used. In contrast, second and third generation biofuels enable the usage of almost all parts of plants. However, the commercial production of second and third generation biofuels is not yet economic due to the complexity and expense of the production.

In the wide and fast developing field of biofuel research, scientists are looking for new suitable feedstock for biofuels production. Furthermore, they are focused on improving already existing but promising techniques. There is a high potential using Berghof highpreactor in science to support the development of new raw material conversion possibilities or finding new catalysts.

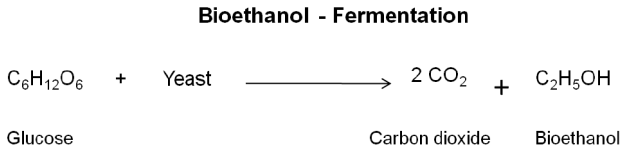
1 First generation biofuels

The feedstock for first generation biofuels is almost entirely composed of sugar, starch or vegetable oils and animal fats, *e.g.* soybeans, rapeseed palm oils, beef, sheep tallow and poultry oil or recycled greases.

Considering the increasing global population, food shortage, and rise of prices usage of food crops, as part of the human food chain, for biofuel production is controversial. But nevertheless, the most common biofuels are produced from conventional raw material.

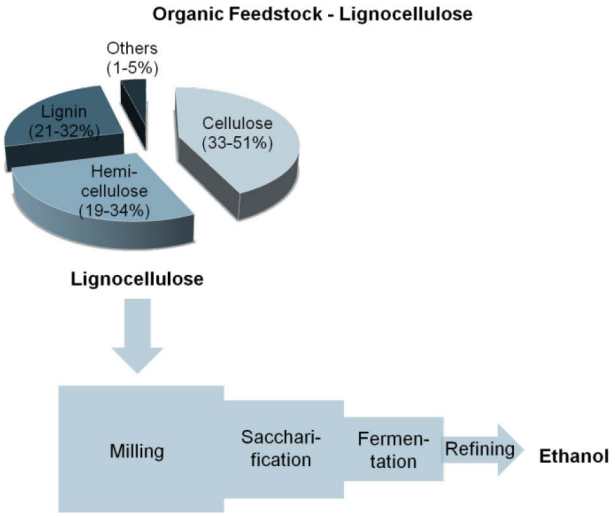
1.1 Bioethanol Production

Bioethanol is produced by enzymatic hydrolysis of crops converting the high sugar content into alcohol.



Fermentation process for the production of bioethanol

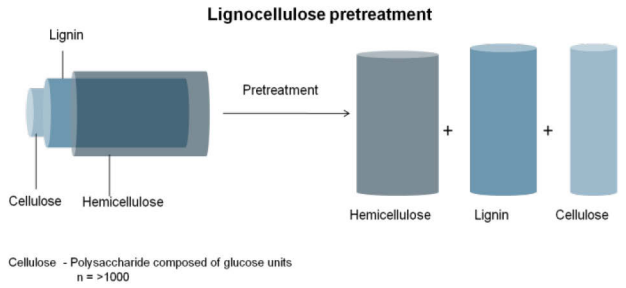
The crucial step is the pretreatment of the lignocellulosic biomass into cellulose and its monosaccharide components (saccharification), which can be economically fermented into ethanol. Normally, hydrolysis of cellulose is difficult due to the strong crystalline structure of cellulose and the presence of lignin. During the so-called delignification, hemicellulose and parts of the lignin are removed from the feedstock *(see also application report "Biomass Pretreatment Technologies")*. The resulting structural change, increased surface area, and increased pore volume of pretreated biomass makes cellulose accessible to enzymes for achieving an economical yield of fermentable sugars.



Lignocellulose as basic raw material for bioethanol production

The most common pretreatment techniques can be divided in different categories:

- → Physicochemical (steam pretreatment, hydrothermal pretreatment)
- → Chemical (organosolv, alkali, dilute acid)
- → Physical
- → Biological
- → Electrical



Fractionation of lignocelluloses in its components

Physicochemical pretreatment

One possibility to treat lignocellulosic raw material is the so called steam explosion. It is normally initiated at 160-260 °C at corresponding pressure of 5-50 bar. The mixture, composed of water vapour and biomass, is held for some seconds or minutes to promote the cellulose hydrolysis. Afterwards, the sample is immediately exposed to atmospheric pressure leading to an explosive decompression. Steam explosion pretreatment is very cost-effective (low energy consumption, no recycling) and starts to become a favored pretreatment technique.

An alternative method presents the carbon dioxide explosion using supercritical carbon dioxide (see also application report "Supercritical Fluids"). In comparison to steam explosion lower temperatures (31.1 °C, 74 bar) are required. Supercritical fluids are solvents in gaseous form which, compressed at temperatures above the critical point, convert into a liquid-like fluid.

As well, working with subcritical water seems to be a promising pretreatment technique. Sub-critical water is defined as liquid water under pressure and temperatures between the boiling point (100 °C, 1 bar) and its critical temperature (374 °C, 221 bar). Within this range hydrogen bonds break down resulting in a change of the properties - subcritical water is less polar and behaves more like an organic solvent. Due to the increased solubility of organic materials and gases the water itself can act as a pseudo-organic solvent, reagent and catalyst in industrial and analytical applications. (see also application report "Supercritical Fluids")

Berghof highpreactor can be used to perform the different techniques of physicochemical pre-treatment of lignocellulose. For reactor configuration it should be noted that a pneumatic valve (nominal width 4.75 mm, flow rate 160 L at 40 bar) is needed to assure safe and fast ventilation in less than 0.5 sec. When performing reactions with supercritical CO_2, the usage of Viton-O-Rings for sealing is not recommended. PTFE or NBR O-Rings are more suitable for this kind of application.

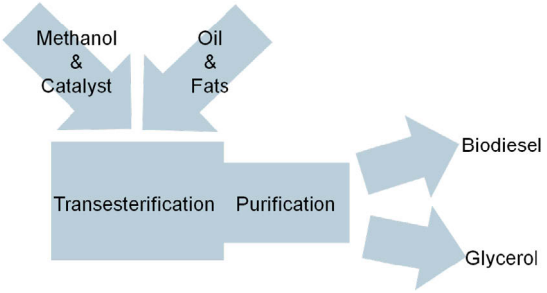
Chemical pretreatment

Organosolvation is a promising chemical pretreatment strategy. Lignocellulosic raw material is treated with an organic solvent mixture (methanol, ethanol, acetone, ethylene glycol) and inorganic acid catalyst (HCl, H_2SO_4) to break the crystalline structure of lignocellulose. The reaction conditions vary in dependence on the biomass. Typically, the reaction is performed at 180-200 °C within 30-90 min.

The increasing demand of Bioethanol cannot durably be covered by crops. Limitations of cultivable land, ecological problems and the interference with the food product market clarify the necessity of new feedstock.

1.2 Biodiesel Production

Biodiesel can be defined as a mixture of Fatty Acids Alkyl Esters (e.g. FAME for Fatty Acid Methyl Ester, or FAEE for Fatty Acid Ethyl Ester) derived from renewable lipid containing raw material, e.g. soybeans, rapeseed palm oils, beef or sheep tallow and poultry oil. The source for its production is chosen according to the availability of feedstock in each country.



Steps for Biodiesel production

Biofuels are biodegradable, non-toxic and low emitting. But however, biodiesel is due to economic reasons the most common biofuel in Europe.

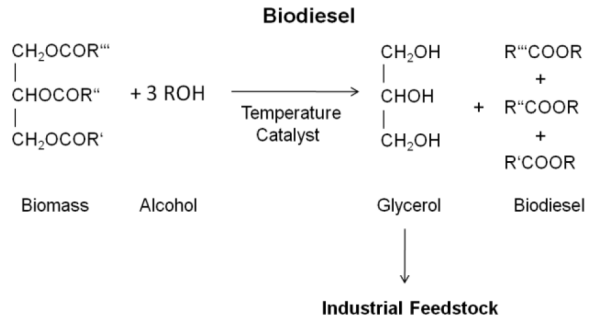
Vegetable oils have the same properties as fossil diesel and could be in general used in its pure form as a fuel. But, plant oil contains free fatty acids, phospholipids, sterols, water, odorants and other impurities which would require modifications of the engine. Additionally, the high viscosity and the low stability against oxidation lead to an incomplete combustion and the formation of high amounts of ashes restricting a long-term usage. Therefore, pretreatment of oil is necessary to make it applicable as fuel.

For the conversion of oil into fuel four major techniques are applied, namely:

→ Transesterification
→ Blending
→ Pyrolysis
→ Micro-emulsion

Transesterification

Transesterification of oil is the method of choice for a cost-effective industrial production of bio-diesel. The fuel is synthesized by converting fat and oil with alcohol in the presence of a catalyst to form fatty acid alkyl esters and glycerol. The low viscosity of the end product is achieved by the removal of glycerol as the component with the highest viscosity.



Transesterification as key step for biodiesel production

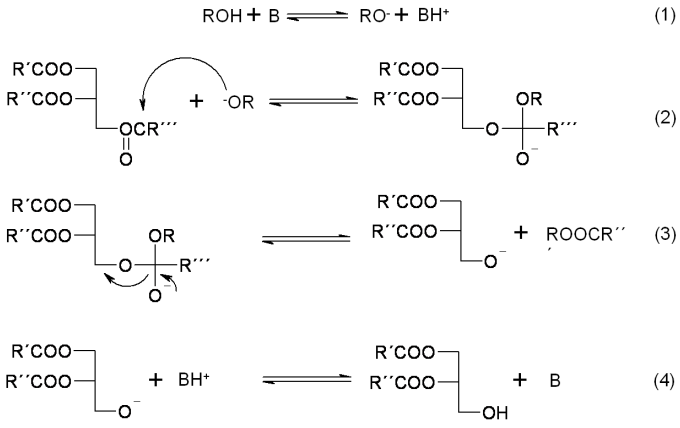
In general, transesterification is carried out by different catalytic processes:

- → alkaline catalysis
- → acid catalysis
- → enzymatic catalysis (lipase)
- → solid phase catalysis

Alkali catalyst

The most commonly used catalysts for alkali-based transesterification reactions are sodium hydroxide or potassium hydroxide in the presence of methanol or ethanol. In contrast to acid-based reactions, the conversion proceeds fast and corrosion is avoided.

Drawbacks are caused by the presence of water leading to an unwanted formation of soap. Saponification lowers the yield of the ester as well as the effectiveness of the catalyst.



Alkali-based transesterification

The mechanism of the acid-based transesterification can be described as followed:

- → Reaction of the base with the alcohol leading to formation of an alkoxide and the protonated catalyst. (1)
- → Formation of a tetrahedral intermediate due to nucleophilic attack of the alkoxide at the carbonyl group of the fatty acid. (2)
- → Formation of alkyl ester and the corresponding anion of the diglyceride. (3)
- → Deprotonation of the catalyst leading to degeneration of the active species. (4)

The conversion of di- and monoglycerides starts with a new catalytic cycle leading to the formation of alkyl esters and glycerol. The reaction takes place at around 60 °C (<10 bar) within 1-2 hours.

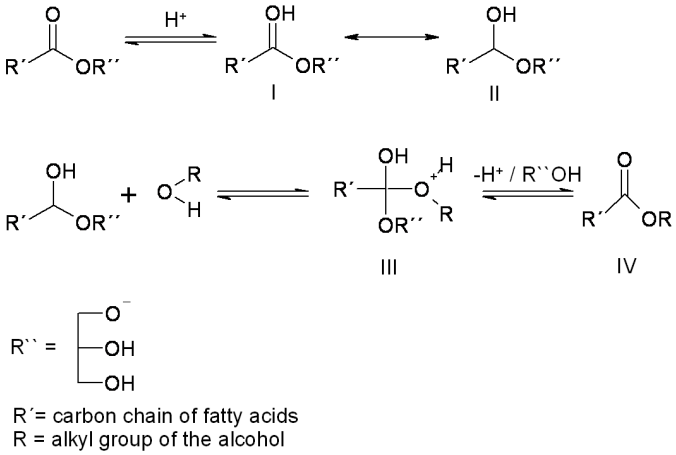
Acid catalyst

Acid-based transesterification is less popular for utilization on industrial scale than alkali catalysts due to a much slower reaction rate and stronger corrosion. Mostly, sulphuric acid, sulphonic acid, phosphoric acid or hydrochloric acid in the presence of methanol is used as a catalyst.

Berghof high*preactor* is characterized by the unique and complete PTFE-lining enabling the support of reactions carried out under extreme corrosive conditions (*e.g.* acid-based transesterification).

Acid-catalyzed transesterification is attractive for the conversion of raw material containing a high content of free fatty acids (algal biomass) and water. Therefore, it is suitable for low-cost lipid feedstock, like cooking oil or grease.

Moreover, soap formation is avoided due to higher temperatures and a higher substrate molar ratio.



Acid-based transesterification

The mechanism of the acid-catalyzed transesterification can be described as followed:

- → Protonation of the carbonyl group of the ester.
- → Formation of carbocation.
- → Formation of a tetrahedral intermediate due to nucleophilic attack of the alcohol.
- → Esterformation by elimination of glycerol and regeneration of the acid catalyst.

The temperature is typically chosen above 100 °C (>50 bar) to reduce the reaction time to a few hours (2-3 hours). High pressure equipment is needed to handle vapor pressures of involved

solvents and acids. At temperatures comparable to the base-catalyzed transesterification (60 °C), a complete conversion would take 1-2 days.

Homogeneous catalyzed transesterification using alkali or acid catalysts are energy consuming and expensive due to secondary reactions and the large amount of waste water produced during separation and cleaning of the catalyst.
Heterogenous catalyzed transesterification using reusable solid catalysts seems to be a promising alternative which could lead to cheaper production costs. Berghof highpreactor can support the search for novel applicable solid catalyst, *e.g.* zeolites. The easy exchangeable teflon-lining minimizes the risk of cross-contamination. Effects like carry-over or contamination by the catalyst can be avoided.

Unique PTFE-lining for high quality products in chemical synthesis

2 Second generation biofuels

With respect to the intervention in the human food chain by using first generation biofuels, non-food alternatives are needed. The feedstock for second generation biofuels comprises waste and cellulosic biomass, e.g. stalks of wheat, corn or wood.

Researchers are asked to identify and characterize plant species that are useful bioenergy crops. This also includes genetic modifications with a lower lignin and higher sugar content or modifications in lignin composition enabling easy delignification.

Currently, some new biofuels are on the stage of development but not yet available. Advanced technologies enable the usage of cellulosic materials for bioethanol production, e.g. non-food crops or plant waste. Nevertheless, obtaining glucose from cellulosic raw material is still a technical problem due to missing efficient and stable enzymes being accessible to cellulose.
Biomass-to-liquid (BtL) biofuels can be produced from different organic feedstock and are a promising alternative to conventional fuels. Such synthetic fuels are produced by thermochemical gasification and are especially designed for the requirements of modern motor concepts

3 Third generation biofuels

Biofuel derived from algal oil are a leading process option for non-food crop biofuel production. Algae are photosynthetic microorganisms producing algal biomass by the conversion of sunlight, water, and carbon dioxide.

There are some crucial advantages making algae much attractive as a feedstock:

- → Fast growing
  (Algae can double their biomass within 24 hours)
- → High yield of oil
  (200 times the yield of plant/vegetable oils)
- → Certain algae types comprise up to 40 % of their overall mass by fatty acids
- → Short harvesting cycle allowing continuous harvests throughout the year
- → Large land area is not needed. (1 % - 3 % of the total U.S. crop area would be sufficient to produce algal biomass that would satisfy 50 % of U.S. transport needs.)
- → No affection of fresh water resources

Energy security politics and an increasing environmental awareness put severe pressure on airline companies. Research on algal fuels is strongly supported with the long-term goal of the successive replacement of kerosene by algal fuel aiming at the reduction of carbon dioxide emission. Lately, the U.S. military began large-scale production of oil from algae into jet fuel.

But however, the development of algal fuels on an industrial scale is in the early stages and disadvantages like high operation costs, high energy input, and efficient harvesting techniques have to be overcome.

4 Literature Overview

Review

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