Polish Journal of Chemical Technology, 13, 1, 58 — 62, 2011, 10.2478/v10026-011-0012-y

Possibilities of utilizing the solid by-products of biodiesel production – a review

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As a consequence of the intended rise in the volume of the biodiesel produced by the member states of the European Union, predominantly from rapeseeds and sunflower seeds, the quantity of the by-products being generated, *e.g.* glycerol, rapeseed/sunflower seed straw and rapeseed/sunflower seed meal, will increase dramatically. It is therefore recommendable to find effective methods for their processing or utilization in order to reduce the costs of biodiesel production without polluting the environment by excessive wastes. As the utilization of glycerol has often been addressed in the literature[1], the aim of our study is to describe the potentiality for utilizing the solid by-products of biodiesel production, namely rapeseed/sunflower straw and rapeseed/ sunflower seed meal.

Keywords: renewable energy, biodiesel, rapeseed straw, rapeseed meal, sunflower seed meal, white biotechnology.

INTRODUCTION

The world energy demand continues to increase. In order to reduce dependency on fossil fuels and decrease the environmental pollution, it is necessary to search for alternative fuels. Biofuels – solid, liquid, or gaseous - are currently the only direct substitute for fossil fuels available on a significant scale[2]. In the EU, according to the biofuels directive (2003/30/EC of 8 May 2003) a 2% market share was targeted for biofuels in 2005 and 5,75 share in 2010[3]. In the transportation sector, the directive 2009/28/EC of 23 April 2009 set the target for biofuels usage of 10% by the end of 2020 (at present it is 4,7%).

Biofuels include e.g. biodiesel, bioethanol, biomethanol, biogas, biohydrogen, bio-ETBE and bio-MTBE[4]. Although the world's biofuel market has been dominated by bioethanol, in the European Union preference is still being given to biodiesel. Currently, 80% of EU biofuels consumption in the transport sector is biodiesel and 20% bioethanol[3]. Biodiesel defined as the fatty acid alkyl monoesters derived from renewable feedstocks, such as vegetable oils, animal fats or recycled fats and oils of diesel quality[3, 5] has became more attractive recently because of their environmental benefits and the fact that it is made from renewable resources.

The chemical composition of biodiesel is dependent upon the feedstock from which it is produced, as vegetable oils and animal fats of differing origin have dissimilar fatty acid composition. The fatty ester composition of biodiesel is identical to that of the parent oil or fat from which it was produced[5, 6]. Feedstocks for biodiesel production vary with the location according to the climate and availability; rapeseed and sunflower oils are principally used in Europe, palm oil predominantly in tropical countries, and soybean oil and animal fats are most common in the USA[7]. In Poland, the annual volume of rapeseed production approaches one million tons. There are, however, potentialities for increasing this quantity to 2.5 million tons per year, of which more than 1.75 million tons could be used for technological purposes, but primarily for the production of methyl esters[8].

The production of one ton of biodiesel requires approximately one ton of rapeseed oil, which is an equivalent of 3.3 tons of rape as a starting raw material. The problem is how to utilize all by-products and wastes obtained, assuming that one ton of the rape seeds processed yields approximately 650 kg of rapeseed meal. It is predicted that the use of another raw material for biodiesel production, *i.e.* sunflower oil, will rise from 59 to 81 thousand tons, which will increase the quantity of the sunflower seed meal available on the market to approx. 200 thousand tons. A rise will also be observed in the quantity of straw, a waste obtained at the first stage of production, *i.e.* at rapeseed or sunflower seed harvest.

The volume of the generated solid wastes will increase with the ever growing biodiesel oil production. That is why the problem of finding a cost-effective, and simultaneously an environmentally sustainable method for the utilization of those wastes has taken on a sense of particular significance.

The aim of this study is to review the recent trends in the utilization of straw and rapeseed/sunflower seed meals, the by-products of biodiesel manufacture from rapeseed oil and sunflower oil.

STRAW UTILIZATION

Rape/sunflower straw is a by-product of rape/sunflower cultivation aimed at obtaining rape/sunflower oils for the needs of oil industry and biodiesel production.

Straw used in agriculture and food processing

Straw serves various useful functions. Produced from oilseed plant, straw can be used as bedding for farm animals or as an additive in fodder. As a source of fibre, it is inferior to crops such as flax, hemp or linseed, but superior to cereal straw. Straw may also be utilized as a compost component or as an additive, improving the humus content of the soil[9]. Stems, petals and leaves of the sunflower contain many valuable components, utilizable as raw materials for the production of foods, fodders, or cosmetics.

Combustion of rapeseed straw

As the composition of rapeseed straw is similar to that of wood and the force required for briquette disintegration is very low[10], one of the possible ways of utilizing this waste material includes combustion, and a big number of farms use straw for heating the living quarters[11]. There are, however, some major disadvantages in this method: the low calorific value (15 MJ/kg) and the high moisture content (30 – 40%) of rapeseed straw. In addition, straw is an expensive fuel, and 15 years of experience have shown that straw is rather problematic as a fuel for heat- and power generation[9]. Metals in ash (in combination with other fuel elements such as silica and sulphur, and facilitated by the presence of chlorine) are responsible for many undesirable reactions in combustion furnaces and power boilers[10]. Co-firing of coal and straw in the existing power plant boilers is proposed as it offers advantages of separate straw combustion[11]. Also the storage of the straw, when use is made of barns with solid roofs, is problematic. Although there is an alternative method which allows straw bales to be stored in large, open, plastic or tarpaulin covered stacks in the field with low storage costs, this is concomitant with feedstock losses[11].

Rapeseed straw as a composite with thermoplastic polymers

It has been found that the wooden parts of rape stems can be a valuable source of lignocellulosic materials which can be used for the manufacture of composites with thermoplastic polymers, such as polypropylene or polyethylene. Polyolefin composites reinforced with natural fibres, *e.g.* rapeseed straw are used in furniture, building and automotive industries[12]. The availability of the inexhaustible and renewable sources, low costs and the recycling opportunity make natural materials very attractive[13]. However, there are some limitations on the wide application of this materials such as the lack of repeatability of chemical composition, the capability of absorbing moisture, the biological degradability and low resistance to high temperature[14].

Straw as a cellulosic material for biotechnological uses

As a lignocellulosic material, rapeseed/sunflower straw contains cellulose and hemicelluloses that are bound together by lignin. Both cellulose and hemicelluloses are polymers built of long chains of sugar monomers, which after pretreatment and hydrolysis can be converted to sugars[15]. While the lignin content represents a potentially large energy source, current techniques involving hydrolysis/enzymatic systems cannot convert the lignin to syngas[16]. Delignification of rapeseed straw under alkaline conditions was found to be inefficient due to a high content of alkali consuming substances. To overcome these difficulties, treatments prior to delignification such as storage on the fields and prehydrolysis have been proposed[17].

An interesting issue addressed in the literature is biorefining based on the separation of the main botanical parts of the crop into different fractions, which can then be used as feedstock for various conventional and new industrial applications[18]. Current research on the biodegradation or bioutilization of cellulose wastes covers the areas specified below.

Biotransformation to fuel

Biofuels are promising substitutes for fossil fuels because they can be produced from biomass which is renewable[15]. Owing to its high content of carbohydrates (more than 60%), rapeseed straw is regarded as an attractive raw material for fuel ethanol production[15, 19]. Bioethanol as a liquid fuel can readily be integrated into the existing fuel supply systems and directly substitute fossil fuels in the transportation sector[20]. Bioethanol production from lignocellulose requires chemical/physical pretreatment to loosen up the lignocellulosic structure and facilitate enzymatic hydrolysis[15, 21]. Biomass pretreatment technology has been widely investigated in recent years and various biological, chemical and physical pretreatment approaches have been proposed to increase the susceptibility of cellulose to enzymatic attack[15, 19]. Hydrolysis can be performed enzymatically or with mineral acids. Since the process conditions for enzymatic hydrolysis and ethanol fermentation are relatively similar, ethanol from lignocellulosic materials can be produced by a simultaneous saccharification and fermentation process[21, 22].

Rapeseed straw is considered as a feedstock for gasification and pyrolysis[11]. The pyrolysis of straw-stalk of rape plants shows the potential of rape plants as an important source of liquid hydrocarbon fuels[23]. Pyrolytic oil is a carbon rich, hydrocarbon mixture bearing oxygen at a considerable ratio and containing ash, sulphur and nitrogen in very small quantities. Rapeseed straw is also a good biomass feedstock for the production of biohydrogen[20].

Production of organic acids

Pentoses (mainly xylose) can be used for the synthesis of fumaric acid. To enhance this process, it is advisable to immobilize the mycelium of the species *Rhizopus arrizus* on appropriate carriers. When use is made of combined saccharification by the cellulases of *T. reesei* and *L. delbrueckii*, the cellulose materials will be efficiently converted to lactic acid[24].

Biomass production

Fungal, bacterial and yeast biomass was produced using the submerged cultures method, as well as cultures in a solid-state medium. Use was made of such strains that had the capacity for degrading cellulose and hemicelluloses, and in some instances also lignin. Upon hydrolysis of polysaccharides to monosaccharides and after making up the hydrolysate with nutrients, yeasts of the genus *Candida* were cultured, which yielded the protein-enriched fodder[25].

Sweetener production from hemicelluloses

Using a microbiological method, it is possible to obtain a sweetener from D-xylose. The sweetener obtained via this route is termed xylitol and can be administered to diabetics as a sugar substitute. The yeast species *Candida guillermondii* has the capacity for a high conversion of xylose to xylitol[24].

Straw as a biosorbent of heavy metals

Vegetable wastes can act as biosorbents of heavy metals carried by a wastewater stream. In order to enhance sorption, the lignocellulose substrate is modified using different methods. However, straw is a biodegradable material, so it will release the heavy metals into the soil in the course of the degradation process[26].

UTILIZATION OF RAPESEED/SUNFLOWER SEED MEALS

The rapeseed/sunflower seed meal, is a by-product from crushing, expelling and extracting oil from oilseed rape/ sunflower. It is solid fraction, with a dry mass content of 90 to 92%. The composition of rapeseed meal widely vary based on the quality of the seed, the method of oil extraction, storage parameters, etc.[27]. It is composed of (%): protein, 30.5 – 32; crude fat, 12.6 – 18, and crude fibre, 10 – 13.8[28, 29].

The pertinent values for the sunflower seed meal (%) are: protein, 27.5; crude fat, 15.0, and crude fibre, 25.0[28]. In dehulled sunflower seed meal the protein content is higher (40%) and fibre content is lower (10%)[30].

Rapeseed and sunflower seed meals as fodder supplements

Owing to the high protein and fat content, as well as the well-balanced amino-acid composition, rapeseed and sunflower seed meals are regarded as valuable fodder supplements in stock-breeding, particularly in pig, poultry, ruminant and fish farming[28]. However, the high content of lignin and cellulose, and the glucosinolate content is a major limiting factor in the feeding of young farm animals[29]. Another limiting factor is the low level of threonine and lysine. It is therefore recommended that the proportion of the rapeseed/sunflower seed meal in the fodder for the fattening pig should not exceed 15%. As a consequence of the chemical changes occurring in the fat fraction, the storage life of the rapeseed/sunflower seed meal ranges between two and three months only.

Rapeseed and sunflower seed meals as energy sources

In the past 10 years, many farms and individual dwellings have switched from hard coal to firewood, wood waste briquettes and pellets[31]. In a pellet form, both meals can be used as combustibles, owing to their high calorific value, which is 26 MJ/kg and 19 MJ/kg for rapeseed meal and sunflower seed meal, respectively. They can also be used in composites with products of a higher calorific value, such as coal or heating oil[32]. However, no cost-effective, environmentally sustainable technology has been reported so far for the combustion (or co-combustion) of rapeseed meal or sunflower seed meal in order to obtain energy.

The literature contains references to their use for the liquid fuel production by pyrolysis. The calorific value of the fuel amounted to 33.7 MJ kg^{-1} [33] or 24 MJ kg^{-1} [34]. Using pyrolysis, it is also possible to obtain charcoal from rapeseed plant straw-stalk[23].

Rapeseed meal as a source of proteins and amino acids

In the search for new protein products for human consumption, defatted rapeseed meal has been considered as a potential source of food-grade proteins because of its well-balanced amino-acid composition[35]. However, the meal contains many undesired components, especially phenolic compounds, among which phenolic acids and condensed tannins are predominant. The high levels of phenolics may be responsible for the dark colour, bitter taste and astringency of the rapeseed meal. Since phenolic acids and condensed tannins may both form complexes with proteins, it is necessary to break phenolic-protein complexes *i.e.* through a system that combines a series of chemical treatments with membrane processing[36], and then to separate the released phenolic compounds from the proteins[36, 37].

Rapeseed as a source of antioxidants

It has been found that phenolic compounds derived from rapeseed are able to effectively prevent lipid oxidation in rapeseed oil[38]. Therefore, extracts from the by-products of rapeseed oil processing can be used to stabilize the refined oils with low amounts of endogenous phenols. This concept can be applied to the commercially refined rapeseed oils after the processing to stabilize the oils with antioxidants naturally present in rapeseed. Antioxidants from rapeseed extracts can also be used in various foodstuffs instead of the commercial ones.

Rapeseed/sunflower seed meals as carbon and energy sources in biotechnological processes

Being rich in protein and fat, with a well-balanced amino-acid composition, rapeseed/sunflower seed meals can be used as both carbon and nitrogen sources in the biosynthesis of valuable metabolites. These have been utilized for the fermentative production of enzymes, antibiotics and mushrooms.

Rapeseed meal has been used as a substrate for xylanase production by *Trichoderma reesei*. Maximum xylanase activity amounted to 210 IU/ml and was obtained within 9 to 12 days[39]. Another reported use of rapeseed meal in phytase production during solid state fermentation by *Aspergillus niger*[40] and by *Aspergillus ficuum* NRRL 3135[41].

Sunflower seed meal has been used as a substrate for the production of enzyme α-amylase with *Bacillus licheniformis*[42] and pharmaceuticals: Cephamycin C with *Streptomyces clavuligerus*[43] and clavulanic acid with *S. clavuligerus*[4]. When added as a supplement to the production medium with spent rice straw, sunflower seed meal enhanced mushroom production[45].

In recent years, research has been conducted on the applicability of rapeseed meals in the biosynthesis of organic acids. The rapeseed meal was found to be an effective medium for *A. niger* in the synthesis of oxalic acid by solid state fermentation, and the maximum concentration of the product approached 150 g kg^{-1} dry weight. The bioprocess was characterized by high chemical selectivity as only oxalic acid was found in the post fermentation media[46].

CONCLUSIONS

The rate of biodiesel production continues to increase. Internationale Grains Council indicated that rapeseed oil was the predominant feedstock for the worldwide biodiesel production in 2007 (48%, 4.6 million metric tons[6]), and it seems that this trend will be continued. It has necessitated the development a thorough search for the cost-effective and environmentally sustainable methods for the utilization of the generated by-products, such as rapeseed/ sunflower straw and rapeseed/ sunflower seed meal. In addition to the conventional use of those lignocellulosic materials for heat generation or in stock-breeding, there are new recommendable methods of their utilization. The most promising one is the so-called white biotechnology which offers potential benefits with regard to economic and environmental protection. Bioprocesses could be useful to biorefinery as an important means to the excessive by-products disposal problem with a potential for revenues from the value-added products. With regard for solid consistency of these by-products, the solid state fermentation method is especially recommended for this purpose. Summarizing, white biotechnology enables, on the one hand, the utilization of the by-products from biodiesel production as substrates, which reduces the production costs of the main product, and, on the other hand, the biosynthesis of valuable products such as enzymes, pharmaceuticals, chemicals or organic acids, which makes possible to replace the conventional chemical methods of their production.

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