Advanced biodiesel from a by-product of refined oil production

The decarbonisation of the transport sector is a major challenge. Biodiesel is a green fuel that could play a significant role in our climate ambitions. To ensure the development of this fuel, Professor Valdis Kampars and his team at Riga Technical University, Latvia, have developed an innovative method for the production of biodiesel. Their process offers advanced biodiesel production from rapeseed oil ‘soap-stock’ (SS), a low-value by-product obtained in the production of refined vegetable oil. Their method requires a shorter processing time and lower energy consumption in comparison with conventional methods of biodiesel production from non-food materials.

Biodiesel is one of the three most important biofuels. It is currently produced mainly from vegetable oil, a feedstock for the food industry. Going forward, the aim is to reduce this share and replace it with biodiesel from non-food raw materials. It is estimated that advanced biofuel should provide around 3.5% of the energy consumed in the transport sector and the ever-increasing demand for biodiesel will require scientists to explore different production avenues. According to a directive from the European Commission on the promotion of the use of energy from renewable sources, the EU transport share of renewable energy in the final energy consumption sector must be at least 14% by 2030.

Advanced biodiesel can only be produced from non-food raw materials, such as used cooking oil, tall oil and also rapeseed oil ‘soap-stock’ (SS). A low-value by-product obtained during refined vegetable oil production, SS is an optimal source of advanced biodiesel. It contains a significant quantity of free fatty acids (FFA) and mono-, di- and tri-glycerides (MG, DG and TG, respectively). Professor Valdis Kampars and his team at the Institute of Applied Chemistry of Riga Technical University, Latvia, have optimised an innovative method for the production of biodiesel from SS through a process that can be completed in as little as three stages.

A NEW USE FOR RAPESEED OIL PRODUCTION RESIDUE

Kampars and his collaborators have presented their method in 2021 at the 29th European Biomass Conference and Exhibition (EUBCE). Until now, the technology to process the conversion of SS into biodiesel has not been extensively scaled, because of the composition of the feedstock, a complex and heavy aqueous lipid emulsion containing water, glycerides, FFA, phosphatides, pigments and other minor non-polar compounds.

The first step in the processing of rapeseed oil SS involves acidification, to achieve removal of undesired phospho-lipids and obtain a mixture of MG, DG, TG and FFA (acid oil, AO). In the following esterification with methanol the obtained product is converted to the mixture of fatty acid methyl esters (FAME), MG, DG and TG. In the last stage MS, DG and TG are transesterified to FAME and advanced biodiesel is obtained. Kampars and his team propose an innovative three-stage process for advanced biodiesel production from soapstock, aiming to ensure the highest possible yield of FAME. In a three-step process, the yield of FAME is about 82% of the theoretically possible.

The proposed three steps include:
1) Synthesis of quality acid oil from SS through acidification; 2) Esterification of the acid oil with methanol in the presence of sulfuric acid; 3) Transesterification of the obtained MG, DG, TG with methanol in the presence of a basic catalyst.

ACIDIFICATION OF FREE FATTY ACID SODIUM SALTS

The SS is heated to 60°C and acidified with 3% H2SO4 in distilled water.

Following the addition of acid, the mixture is heated at 90°C for 1 hour. After cooling, the reaction mixture is divided into two layers. The upper dark brown layer is lipid and fatty acid rich phase and bottom light brown layer is water phase. The waste water layer is discarded, while the upper acid oil layer is further processed.

ALKALI CATALYSED TRANSESTERIFICATION REACTION

The FAME/glyceride mixture is heated to 55°C and then sodium methoxide is added (1.5% of TG mass) in methanol (methanol:TG molar ratio 9:1) was added. The reaction mixture is heated at 55°C for 1.5 hours and allowed to cool down and separate into two layers. The upper dark brown layer is FAME and the bottom black layer is made of glycercine layer and impurities. The glycercine layer can be discarded and the FAME layer further purified.

ADVANTAGES OVER OTHER METHODS

The advanced biodiesel synthesis in three stages (acidification, esterification, transesterification) from rapeseed oil soapstock offers numerous advantages. Obtaining the acid oil from SS with the method proposed by Kampars, requires a shorter processing time and low energy consumption. The production of acid oil by conventional methods requires at least 4 hours and a temperature of up to 120°C (195°C in the absence of a catalyst).

The most promising sources for advanced biodiesel include feedstock that’s unsuitable for food, such as by-products of rapeseed oil production.
Soapstock could become an important raw material for biofuel production. In the conventional process, the fuel use of a homogeneous base catalyst which cannot be separated and reused. After neutralisation, it is separated in form of salts, however, part enters the product and requires washing the raw biodiesel with water, which causes wastewater treatment. Extensive research is being conducted in all these areas, and is also being carried out by the team at Riga Technical University. For example, the researchers have investigated the possibility of replacing TG transesterification with methanol with interesterification with methyl acetate. This would allow the synthesis of triacetoxy instead of glycerol, which can be incorporated into biofuel and would increase its yield. Unfortunately, despite the interesting results, it was not possible to develop a technology that would have found widespread use. The same is true of other attempts to improve the conventional process and number of individual stages increase. The raw materials costs decrease, but production costs increase. It is necessary to separate those raw material components that cannot be used in FAME synthesis and to look for ways to convert to FAME the useful components with high yield. As in the case of SS, the useful components are MG, DG, TG and FFA. The increased content of FFA in the raw material precludes the use of homogeneous basic catalysts, as soap is formed and the FAME layer does not separate. Several variants remain, of which FFA esterification with subsequent MG, DG and TG transesterification is best realised.

The base of cheap and non-food raw materials is very limited. Currently, the most important raw material in the EU is used cooking oil, which could provide about 20% of the biodiesel currently produced. The amount of biodiesel produced on the basis of other raw materials (tail oil, animal fats, oil production and food waste) is significantly lower. Therefore, the development of production technology for any raw material is becoming increasingly important.

CONCLUDING REMARKS
Professor Kampars and his team at the Technical University in Riga have developed a process of biodiesel synthesis from low quality rapeseed oil. The proposed process just requires simple chemical methods, inexpensive reagents and mild conditions. The obtained biodiesel has a high FAME content (94.8%) and good overall yield (approx. 82% of theoretically possible). The advanced biodiesel product obtained can be used in blends with biodiesel, petroleum diesel or further refined to meet the required standard. Since the worldwide production of vegetable oil exceeds 200 million ton per year, soapstock could become an important raw material for biofuel production. Further studies to optimise the reactions conditions are being conducted at the Kampars laboratory, with the aim of increasing the yield of the process and improving of quality of the obtained biodiesel.

Professor Valdis Kampars and his team propose an innovative three-stage process for advanced biodiesel production from soapstock. The reactions can be conducted at low temperature and pressure. The proposed process just requires simple chemical methods, inexpensive reagents and mild conditions. The obtained biodiesel has a high FAME content (94.8%) and good overall yield (approx. 82% of theoretically possible). The advanced biodiesel product obtained can be used in blends with biodiesel, petroleum diesel or further refined to meet the required standard. Since the worldwide production of vegetable oil exceeds 200 million ton per year, soapstock could become an important raw material for biofuel production. Further studies to optimise the reactions conditions are being conducted at the Kampars laboratory, with the aim of increasing the yield of the process and improving of quality of the obtained biodiesel.

Professor Kampars teaches both undergraduate and graduate students. He has published almost 96 scientific papers. Professor Kampars explores new methods for the production of biodiesel.

Reference:
