0. Introduction

“PROMOFUEL” is a research project for the development of advanced biodiesel fuels, whereby the consortium consists of three experienced partners in the field of biofuels. The project is focusing on new non-food feedstocks for biodiesel production, which until today are mainly excluded from the traditional biodiesel production because of the chemical properties of these feedstocks. Most of the non-food feedstocks for biodiesel production like microbial oils, Jatropha, Camelina etc. contain fatty acids with high unsaturation, leading to low oxidation and storage stability. The project will bring new understanding of the relation between chemical composition and fuel behavior. Two biodiesel test fuels were prepared in larger scale out of rubber seed oil and fish oil. These oils are chosen as representatives of non-food feedstocks or microbial oils. With the test fuels engine and emission tests were carried out and the mutagenicity of the emissions are tested in order to get a better understanding of the influence of the chemical structure on the toxicity of particulate emissions. Laboratory tests have been carried out with partial hydrogenation in order to enhance the oxidative stability and to increase the shelf life. The results of the project are disseminated in a final workshop and will be the basis of further development and research on advanced biofuels between Europe and Korea.

The two main objectives of “PROMOFUEL” are developing scientific facts for the suitability of new non-food feedstocks for traditional biodiesel production and to get better knowledge on the influence of the type of feedstock on environmental and health effects of engine emissions.

The goal is to enhance the feedstock variability for traditional biodiesel plants, where huge investments have been done within the last years. The production of fatty acid methyl esters (FAME biodiesel) today is still the most economical way for the production of alternative diesel fuel, the technology is well established and there is already a huge infrastructure of biodiesel plants existing worldwide. However, due to the lack of sufficient sustainable feedstocks there is a huge overcapacity of biodiesel production units especially in Europe.
Expectations for new technologies for alternative diesel fuels like biomass to liquid (BtL) could not been fulfilled until now because of serious technological and logistical problems. Hydrotreated vegetable oils are already produced in industrial scale they could be used for aviation fuel or as admixture for diesel fuel, leading to even higher blends as B10. However, these technologies need high investment and also running costs because of more sophisticated technology. Furthermore, until now only food grade vegetable oils can be applied for this technology, leading to higher production costs than traditional biodiesel, so the future is rather uncertain. The strategy of the project is to establish criteria for the use of new non-food feedstocks, which normally contain higher amounts of higher unsaturated fatty acids like linoleic and linolenic acid as well as polyunsaturated fatty acids. Most of new

potential seeds like Jatropha, Camelina or other potential crops contain higher amounts of linoleic and linolenic acid, which limits the use of these feedstocks in higher extent because of regulations in internal specifications. Also oil from microalgae or other micro-organisms, which are supposed to be the most promising feedstocks for biofuels in the future, contain fatty acids with high unsaturation, even fatty acids with 5 or more double bonds. Within this project two representatives of these feedstocks are selected for basic investigation, rubber seed oil and fish oil. Rubber seed oil stands for oil with higher amounts of linoleic and linolenic acid, whereas fish oil can be seen as model substance for micro algae oil, because micro algae are the main feed for fish. The main objections for these feedstocks for biodiesel production are the poor oxidation and storage stability resulting from high unsaturation. To overcome these problems within this project it should be tested, what maximum amount of unsaturated products could be blended with mineral diesel in order to meet EN 590. Furthermore partial hydrogenation of the double bonds of these high unsaturated feedstocks should be carried out in order to get products, which are more stable but still have very good cold temperature behavior. Such a strategy is far more economic than total hydrogenation, which additionally needs a step of hydro isomerization which only can be done in specified plants.

However, the technical suitability of an advanced fuel cannot be the only parameter of judgment: Availability of feedstocks as well as sustainability including emissions and especially health effects must be taken into account, too.

Therefore, the other main objective of “PROMOFUEL” was to monitor the state of the art knowledge on emissions and health effects relative to different biodiesel feedstocks and engine conditions.

Limited knowledge is available on the influence of chemical structure of the different biodiesel feedstocks on the engine and emission behavior. Especially health effects of soot emissions coming from diesel engines are big concern in the overall emission of combustion engines. Mutagenicity tests of emissions with pure vegetable oils, pure biodiesel and blends with diesel fuels have shown that there is a strong difference between the different fuels and blends. Pure vegetable oils seem to have higher mutagenicity than biodiesel and petro diesel, blends of biodiesel with diesel fuel have significant lower mutagenicity, but surprisingly emissions of B20 have higher mutagenic potential than other blends.

Possible reaction products from diesel fuel/biodiesel blends are in the focus of interest. It is well known in literature that emissions especially from B20 (20 % blend of biodiesel in fossil diesel) can lead to a maximum of mutagenicity.

Within this project different biodiesel samples from new feedstocks like rubber seed oil and fish oil were prepared and B20 blends have been used in engine tests. The influence of chemical composition and emissions was studied and the mutagenic potential of the particulate matter is measured and compared with the results of the other feedstocks. So a relation between chemical composition and grade of mutagenic potential of engine emissions should be found.

In the long term, the consortium of KORANET partners wants to understand the interactions between fuels components and their influences on the emissions and especially the health effects. In the future, fuels with high biogenic content shall be designed with regard to the technical, environmental and health-related aspects. So “PROMOFUEL” should develop scientific facts for the promotion of new non-food feedstocks for biodiesel production, on the one side in testing the possibility of finding the optimum blend of higher unsaturated feedstocks or in chemical modification, on the other side finding out the influence of chemical composition on the health effects of emissions.

1. Non-conventional biodiesel sample preparation

1.1. Introduction

In Korea, biodiesel is getting more important because it is recognized as the promising tool to mitigate CO_2 in transport sector. Since the annual diesel consumption in Korea is two times higher than gasoline, implementation of biodiesel has been started since 2006. With strong support from Korean government, the biodiesel production capacity has increased rapidly. Current production capacity of biodiesel in Korea is about 700,000kL/year but the actual production is only 400,000kL/year due to the shortage of feasible feedstocks since most feedstocks consumed in Korea are the imported palm, soybean oils and the waste cooking oil collected in land. The waste cooking oils are also derived from palm and soybean oils. Non-conventional feedstocks like rubber seed oil, fish oil and algal oils are emerging as the promising feedstocks for making biodiesel because they are inedible and may be cheaper than the conventional feedstocks. Another possible feedstock is winter rapeseed which may be cultivated in paddy fields in Korea during winter. Since all those feedstocks considered in Korea are containing high unsaturation fatty acids, evaluation of the biodiesels made from the non-conventional feedstocks as motor fuel will be very important.

The cooperation between Europe and South East Asia and especially Korea in the field of biofuels and biodiesel is very important because South East Asia is the major producer for vegetable oils with long tradition in oleochemical utilization of especially palm oil, but on the other side there is a big demand for feedstocks for biodiesel production. So it is very important to find and develop new non-food feedstocks, so Korea might have a high potential for the production of microbial oils like oil from micro algae. So this project could be the basis for the development of future intensive research in this area.

The objective of the work is the preparation of 20L of fatty acid methyl esters(FAMEs) out of rubber seed oil and fish oil for Partner 1 (University of Graz) and Partner 2 (Coburg University) to do the works, the partial hydrogenation of the FAMEs and the engine tests and emissions. For preparation of non-conventional biodiesel samples, we also established the reaction conditions for conversions of rubber seed and fish oils into FAMEs and analyzed the compositions of the FAMES and their fuel properties

1.2. Materials and Methods

1.2.1. Materials

About 200kg of rubber seeds were purchased from the local company in Thailand. The oil is mechanically extracted from the seeds after dehulling and roasting in Korea. Rubber seed oil extracted was used for preparation of rubber seed fatty acid methyl ester (FAME).
Salmon oil was purchased from a local supplier in Germany and used for making salmon oil FAME.

1.2.2. Pretreatment and Transesterification of Rubber Seed Oil

For the esterification of free fatty acids contained in rubber seed oil, the mixture of oil, methanol and sulfuric acid was mixed in 50L reactor at 65^{o}C for 3 hours (figure 1). The pretreated oil was used for the transesterification. Rubber seed oil was again mixed with methanol and potassium hydroxide at 65^{o}C for 40 minutes.

Figure 1: Reactor for conversion of rubber seed oil into FAME.