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OILSEED RAPE AS FEEDSTOCK FOR BIODIESEL PRODUCTION IN RELATION TO THE ENVIRONMENT AND HUMAN HEALTH

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ABSTRACT

Oilseed rape is one of the most important crops in cultivation process. A current developmental trend in non-food rapeseed production on agricultural land shows that this new course is irreversible and is a great opportunity for agriculture. Non-food rapeseed production is focused on the production of biodiesel. Biodiesel has good environmental properties. Lower emissions are produced by the combustion of biodiesel than for diesel. In content of exhaust gas is observed a significant decrease of polycyclic aromatic hydrocarbons, particulate matter and etc. The analysis of the literary knowledge on impacts of biodiesel on exhaust emissions, on regulated emissions, shows a reduction of 10.1% for particulate matter, of 21.1% for hydrocarbons, and 11.0% for carbon monoxide with the use of B20. Nitrogen oxides (NOx) increased by 2.0%. Biodiesel was introduced into the European market in the 1988s as B100. The use of blends with content up to 5% biodiesel has no significant impact on the emissions and their toxicity. An increased mutagenicity was observed with blends containing 20%. Nevertheless, increased mutagenic effects were observed under specific conditions. Accordingly, the problem concerning blends of diesel fuel with biodiesel (B20) should be investigated with high priority. No comprehensive risk assessment for diesel engine emissions from biodiesel and its blends is possible In regard to a comprehensive hazard characterization it is urged to develop a panel of standardized and internationally accepted protocols which allow a reliable assessment of possible health hazards which may arise from the combustion of new fuels compared to conventional diesel fuel. These methods should be robust and should reflect the various health hazards associated with diesel engine emissions to supplement data on regulated emissions. Methods for the generation of the exhaust and sample preparation should be harmonized. There is sufficient evidence supporting a causal relationship between diesel engine emissions and acute health effects, as are childhood asthma, non-asthma respiratory symptoms, impaired lung function, total and cardiovascular mortality, and cardiovascular morbidity. Although, diesel engine emissions exposures in developed countries changed strongly during recent years, reliable animal experiments or epidemiological studies concerning the use of new fuels and technologies are almost lacking.

Keywords: oilseed rape; energy resource; biodiesel; ecological attribute; environment; human health

INTRODUCTION

Oilseed rape is a major agricultural crop. It has wide application in agriculture, food science and industry. The aim of this paper is to present an overview of current knowledge on the using of oilseed rape for biodiesel production in terms of protecting the environment and human health.

Oilseed rape as feedstock of biodiesel

Diesel engines are important in industry, agriculture and transportation because they have a simple and strong mechanical structure, a low fuel cost and a high thermal efficiency. However, diesel engines are commonly responsible for the emission of large amounts of gaseous and particulate pollutants, which adversely affect health **(Geiss et al., 2010; Wu et al., 2010; Avino et al., 2011).** The gaseous pollutants from diesel engines mainly comprise carbon monoxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx) and hydrocarbons (HC) **(Colbeck et al., 2011; Ma et al., 2011).** Nitrogen oxides are usually generated in combustion at high temperature, and its concentration increases with the engine combustion efficiency **(Yanowitz et al., 2000**). Most sulfur oxides from diesel engines are produced by the high-temperature oxidation of the sulfates in petroleum diesel. After they are emitted into the atmosphere, nitrogen oxides and sulfur oxides become nitrates, sulfuric acid or sulfate aerosols that detrimentally affect the environment. With the Kyoto Protocol, developed countries are to reduce their greenhouse gas emissions in the period 2008-2012 by roughly 5% compared to the 1990 level. Diesel engine emissions are related to quality characteristics of diesel fuels. The main pollutants emitted from diesel engines is unburned hydrocarbons, solid particles, aldehydes, polycyclic aromatic hydrocarbons, carbon monoxide, nitrogen oxides **(Burnete et al., 2008).** The depletion of world petroleum reserves and the increased environmental concerns have stimulated the search for alternative sources for petroleum - based fuel, including diesel fuels. Because of the closer properties, biodiesel fuel (fatty acid methyl ester) from vegetable oil is considered as the best candidate for diesel fuel substitute in diesel engines.

Production capacity in the 27 countries that comprise the European Union in 2008 was estimated by the European Biodiesel Board to be 4.8 billion gallons per year versus 1.4 billion gallons per year in 2006. The continued drive for energy sustainability and independence among energy-consuming countries, governmental mandates for alternative fuel usage and increased global production capacity contribute to the need for alternative sources of biodiesel fuel). By 2012, one billion gallons of biomass-based diesel is required under the renewable fuels standard **(Kotrba, 2008).**

Lastly, the high prices of commodity vegetable oils and animal fats have made exploration of economical alternative non-food feedstock an important research topic. Fossil fuel resources are decreasing daily. As a renewable energy, biodiesel has been receiving increasing attention because of the relevance it gains from the rising petroleum price and its environmental advantages. This review highlights some of the perspectives for the biodiesel industry to thrive as an alternative fuel, while discussing opportunities and challenges of biodiesel. **Lin et al. (2011)** paid attention to overview about developments of biodiesel in past and present, especially for the different feedstock's and the conversion technologies of biodiesel industry. More specifically, an overview is given on possible environmental and social impacts associated with biodiesel production, such as food security, land change and water source. Further emphasis is given on the need for government's incentives and public awareness for the use and benefits of biodiesel, while promoting policies that will not only endorse the industry, but also promote effective land management.

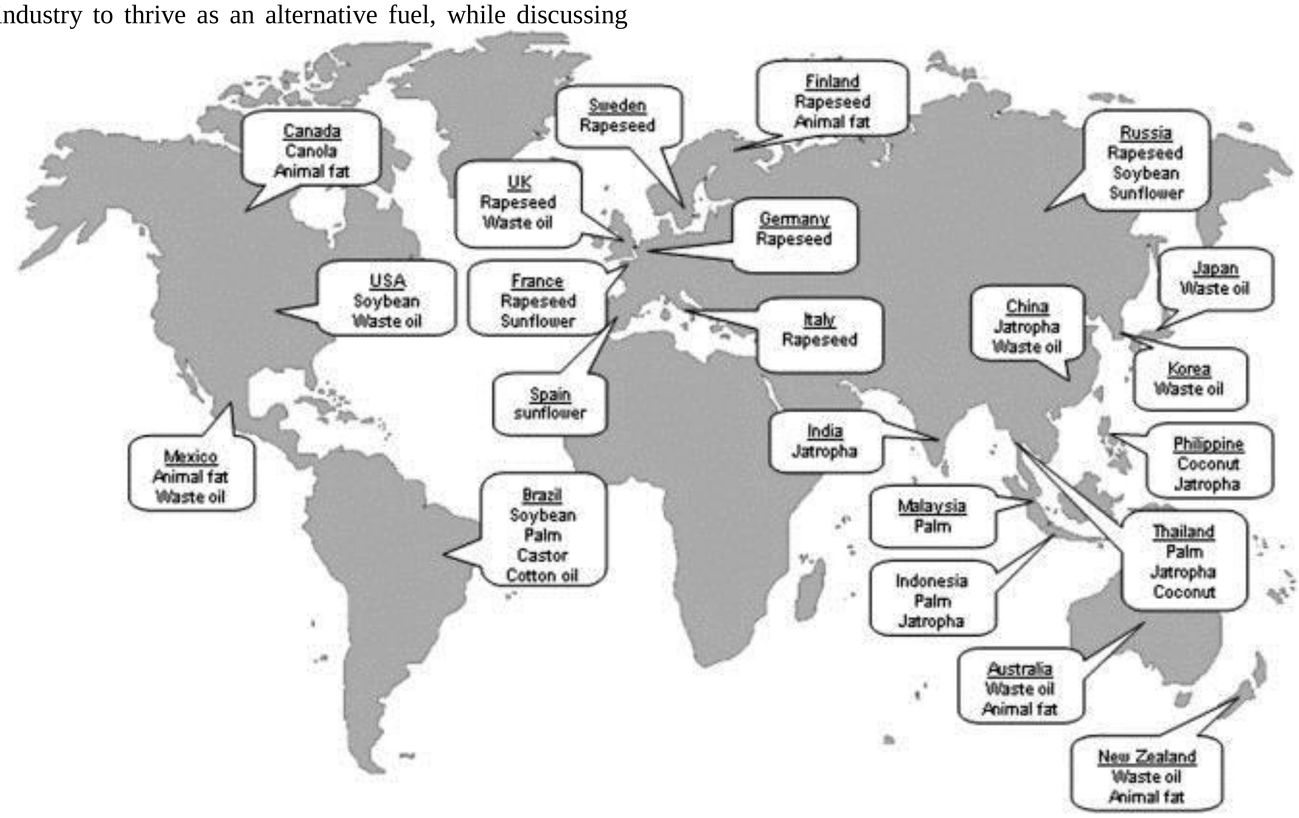

Figure 2 Fatty acid methyl esters around the world (**Lin et al., 2011)**

Table 1 Tests of diesel-engines fuelled with biodiesel in literature, rapeseed oil is use

Species of biodiesels Diesel engines	Types of tested	Measurements	References
Rapeseed-oil-based biodiesel	A heavy duty diesel engine (Model: EURO 2 IVECO 8360.46R) (Six cylinders; Turbocharged with indirect fuel injection; 130 mm bore×112 mm stroke; Max output power: 158 kW)	Total PM; Soluble organic fraction (SOF); Gaseous pollutants (NOx and CO); PAH/nitro-PAH; Carbonyl compounds and light aromatics; Mutagenicity assays; Brake-specific fuel consumption (BSFC)	**(Turrio-Baldassarri et al., 2004)**
Five typical biodiesels (cottonseed oil, (soybean oil, rapeseed oil, palm oil and waste cooking oil)	A Euro-III diesel engine (Model: Cummins ISBe6) (Six cylinders; Turbocharged with indirect fuel injection; Rated output power: 136 kW/2500 rpm)	Total PM; Dry soot; Gaseous pollutants (NOx, CO, and HC)	**(Wu et al., 2009)**

Transesterification reaction of rapeseed oil in supercritical methanol was investigated without using any catalyst. An experiment has been carried out in the batch-type reaction vessel preheated at 350 and 400 °C and at a pressure of 45-65 MPa, and with a molar ratio of 1:42 of the rapeseed oil to methanol. It was consequently demonstrated that, in a preheating temperature of 350 °C, 240 s of supercritical treatment of methanol was sufficient to convert the rapeseed oil to methyl esters and that, although the prepared methyl esters were basically the same as those of the common method with a basic catalyst, the yield of methyl esters by the former was found to be higher than that by the latter. In addition, it was found that this new supercritical methanol process requires the shorter reaction time and simpler purification procedure because of the unused catalyst **(Saka a Kusdiana, 2009)**. In the work, the transesterification reaction of rapeseed oil with methanol, in the presence of alkaline catalysts, either homogeneous (NaOH) or heterogeneous (Mg MCM-41, Mg-Al Hydrotalcite, and K^+ impregnated zirconia), using low frequency ultrasonication (24 kHz) and mechanical stirring (600 rpm) for the production of biodiesel fuel was studied. Selection of heterogeneous catalysts was based on a combination of their porosity and surface basicity. Their characterization was carried out using X-ray diffraction, nitrogen adsorption-desorption porosimetry and scanning electron microscopy with energy dispersive spectroscopy. The activities of the catalysts were related to their basic strength. Mg-Al hydrotalcite showed particularly the highest activity with conversion reaching 97%). The activity of ZrO_2 in the transesterification reaction increased as the catalyst was doped with more potassium cations, becoming thus more basic. Use of ultrasonication significantly accelerated the transesterification reaction compared to the use of mechanical stirring (5 h vs. 24 h). Given the differences in experimental design, it can be concluded that the homogeneous catalyst accelerated significantly the transesterification reaction, as compared to all heterogeneous catalysts, using both mechanical stirring (15 min vs. 24 h) and ultrasonication (10 min vs. 5 h). However, the use of homogeneous base catalysts requires neutralization and separation from the reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy. Heterogeneous solid base catalysts can be easily separated from the reaction mixture by simple filtration, they are easily regenerated and bear a less corrosive nature, leading to safer, cheaper and more environment-friendly operations **(Georgogianni et al., 2009).** The purpose of this work was to examine a heterogeneous catalyst, in particular calcium compounds, to produce methyl esters of rapeseed oil. This research showed that the transesterification of rapeseed oil by methyl alcohol can be catalysed effectively by basic alkaline-earth metal compounds: calcium oxide, calcium methoxide and barium hydroxide. Calcium catalysts, due to their weak solubility in the reaction medium, are less active than sodium hydroxide. However, calcium catalysts are cheaper and lead to decreases in the number of technological stages and the amount of unwanted waste products. It was found that the transesterification reaction rate can be enhanced by ultrasound as well as by introducing an appropriate reagent into a reactor to promote methanol solubility in the rapeseed oil. Tetrahydrofuran was used as additive to accelerate the transesterification process **(Gryglewicz, S. 1999).** Methyl esters of fatty acids are characterized by excellent properties as diesel engine fuels. They have proper viscosity and boiling point and a high cetane number. Methyl esters added to a hydrocarbon fuel reduce the emission of noxious combustion products to the atmosphere **(Chang et al., 1996).** Transesterification can be catalyzed by both acids and bases **(Koskikallio, 1969)** and even enzymatically **(Briand et al., 1991)**. The use of bases is not associated with intensive corrosion of the equipment. The general mechanism of the methanolysis of esters is given in Fig. 1.

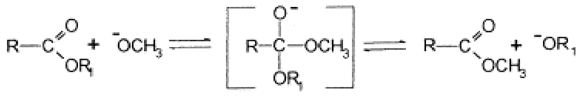

Figure 1 Mechanism of base catalysed alcoholysis of esters **(Gryglewicz, 1999)**

The biodiesel (fatty acid methyl esters, FAME) was prepared by transesterification of the mixed oil (soybean oil and rapeseed oil) with sodium hydroxide (NaOH) as catalyst. The effects of mole ratio of methanol to oil, reaction temperature, catalyst amount and reaction time on the yield were studied. In order to decrease the operational temperature, a co-solvent (hexane) was added into the reactants and the conversion efficiency of the reaction was improved. The optimal reaction conditions were obtained by this experiment: methanol/oil mole ratio 5.0:1, reaction temperature 55 °C, catalyst amount 0.8 wt.% and reaction time 2.0 h. Under the optimum conditions, a 94% yield of methyl esters was reached ~94%. The structure of the biodiesel was characterized by FT-IR spectroscopy. The sulfur content of biodiesel was determined by Inductively Coupled Plasma emission spectrometer (ICP), and the satisfied result was obtained. The properties of obtained biodiesel from mixed oil are close to commercial diesel fuel and is rated as a realistic fuel as an alternative to diesel **(Qiu et al., 2011).**

Biodiesel has similar properties as mineral oil-derived fuel and can be used in pure form (B100) or blended with common diesel fuel at any concentration **(Knothe et al., 2010).** Biodiesel use has been increased in the USA mainly as a 20% blend with diesel fuel (B20), since the “Energy Policy Act” came into force. ASTM D6751-08 details the US specifications for biodiesel blends. Biodiesel was introduced into the European market in the 1988s as B100. In 2003, fuel suppliers were committed to include increasing amounts of renewable fuels in all transport fuel sold in the EU by the **Directive 2003/30/EC**. At the same time, the European Committee for Standardization (CEN) released the standard **EN 14214** for biodiesel which was updated in 2008. Currently, diesel fuel is supplemented with 7% biodiesel (B7) in Germany. Determination of the emissions profile is a key step in assessing the acceptability of a biodiesel fuel produced from a new feedstock **(Michael et al., 2001).** Other authors took a similar position in their studies on research of emissions in this field, too **(Jablonický et al., 2010; Müllerová et al., 2011).**

Biodiesel and human health

Diesel engine emissions are highly complex mixtures. They consist of a wide range of organic and inorganic compounds which are distributed among the gaseous and particulate phases. Public health concern has arisen about diesel engine emissions for these reasons (**HEI, 1995).** Most particles of diesel engine emissions are nanoscaled making them readily respirable. These particles have hundreds of chemicals adsorbed onto their surfaces, including many known or suspected mutagens and carcinogens, e.g. polycyclic hydrocarbons (PAH) and nitrated polycyclic hydrocarbons (nPAH). The gaseous phase contains many irritants and toxic chemicals, e.g. aldehydes. Also nitrogen oxides (NO_x), which are irritants and ozone precursors, are among the combustion products in the gaseous phase. Health Effects Institute has published a series of special reports and research papers - most of the reviews written by interdisciplinary expert panels - dealing with health effects of diesel engine emissions **(HEI, 1999, 2010).** According to these reviews, there is sufficient evidence supporting a causal relationship between diesel engine emissions and acute health effects, namely the exacerbation of asthma. The experts also found a suggestive evidence of a causal relationship with chronic health effects like childhood asthma, non-asthma respiratory symptoms, impaired lung function, total and cardiovascular mortality, and cardiovascular morbidity.

Also in 2002, US-EPA released a Draft Technical Report on impacts of biodiesel on exhaust emissions (**EPA, 2002).** The analysis mainly comprised data on regulated emissions, showing a reduction of 10.1% for particulate matter (PM), of 21.1% for hydrocarbons (HC), and 11.0% for carbon monoxide (CO) with the use of B20. Nitrogen oxides (NO_x) increased by 2.0%. In addition, 11 "air toxics" were evaluated, including mainly small carbonyls and aromatics which are associated with the gaseous phase of the emissions. A small reduction of these compounds was calculated overall. **McCormick (2007)** included more recent data in a short review. He found the evaluation of U. S. Environmental Protection Agency confirmed and added some studies providing results of biological assays showing a reduced mutagenicity.

Health risks from diesel engine emissions were assessed for inhabitants **(Morris et al., 2003).** The alteration of health risk by use of B20 was calculated based on "Unit Risk Factors" of the following six exhaust components: benzene, 1,3-butadiene, acetaldehyde, formaldehyde, standard diesel particles and B20 diesel particles. According to the authors these compounds contribute to 90% of the health risk, which is caused by air pollution in evaluated region and heavy-duty vehicles ought to contribute with 53% to the entire particulate matter emissions of all trucks in this region. B20 would therefore reduce particulate matter emissions by about 5%. According to a calculation of **Lindhjem and Pollack (2000)**, the use of B20 should lead to a reduction of emitted particle mass by 9% and consequently to a reduction of particulate matter toxicity by 5%. Based on these assumptions, **Morris et al. (2003)** estimated that B20 would lead to 2% less deaths if 50% and to 5% less deaths when all of the heavy-duty vehicles were run on B20. The authors of this assessment made several assumptions which cumulate to a considerable uncertainty. Besides the notion that the procedure used in this study is not uniformly accepted and the unit risk factors are already estimates, it is not known if these six compounds really contribute to 90% of the health risk which is associated to air pollution in evaluated region. In addition, unexpected effects occur when biodiesel in certain amounts is added to common diesel fuel (blending). **Krahl et al. (2008)** observed an increase of the mutagenic potency when combusting blends showing the maximum using B20. This effect occurred when biodiesel was mixed with different petroleum-derived fuels and was reproduced using three separate engines.

In several critical reviews of the literature on health effects of diesel engine emissions, Hesterberg and coworkers highlighted weaknesses and shortcomings of the studies on which Health Effects Institute and Environmental Protection Agency conclusions on diesel engine emissions were based (**Bunn et al., 2004; Hesterberg et al., 2005, 2006, 2009, 2010)**. Regarding the epidemiological studies concerning the lung cancer risk the lack of contemporaneous measurements of diesel engine emissions exposures, uncertainties concerning exposure history, and inadequate consideration of confounding exposures such as gasoline exhaust and cigarette smoke were criticized (**Bunn et al., 2004**). Additionally the lacking dose response relationship was pronounced with regard to the observation that underground miners experiencing the highest exposures to diesel engine emissions did not show elevations in lung cancer **(Hesterberg et al., 2006).** Moreover, animal studies showed lung tumors only in rats but not in mice or Syrian hamsters, and in rats only under "lung overload" conditions (**Hesterberg et al., 2005)**. According to clinical and exposure studies showing lung inflammatory effects and thrombogenic and ischemic effects of inhaled diesel engine emissions in humans it was remarked that unrealistically high diesel engine emissions concentrations from older-model diesel engines were used (**Hesterberg et al., 2009)**. Additionally, till now no mechanism of action was established allowing a reliable prediction of adverse health effects of diesel engine emissions and it is uncertain which diesel engine emissions constituents underlie the observed responses. There are necessary the studies for using realistic environmental and occupational exposures from new technology diesel engines including low sulfur fuels and exhaust after-treatment **(Hesterberg et al., 2010).** In fact, during recent years strong efforts were made to minimize diesel engine emissions-related health hazards. This includes improved combustion, exhaust after-treatment, the reduction of sulfur and aromatics, and the introduction of reformulated fuels. Therefore the contemporaneous risk assessment may be based on over-aged data. Hesterberg and coworkers suggest to differentiate "New Technology Diesel Exhaust" (defined as diesel engine emissions) from post-2006 and traditional diesel exhaust (**Hesterberg et al., 2011, 2012; McClellan et al., 2012).** Although, diesel engine emissions exposures in developed countries changed strongly during recent years, reliable animal experiments or epidemio-logical studies concerning the use of new fuels and technologies are almost lacking.

CONCLUSION

The knowledge of the feedstock oilseed rape we can summarize the following points, including perspectives its use in the EU:

a) Oilseed rape is suitable feedstock for biodiesel production.

b) Biodiesel of rapeseed oil includes energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

c) Biofuels have to meet certain criteria to count against the 10% goal. In the Renewable Energy Directive, specific sustainability requirements are laid out. These include minimum greenhouse gas emissions reductions, land use and environmental criteria as well as economic and social criteria, and adherence to International Labor Organization conventions. The European Commission is reportedly working on updating the default values on greenhouse gas emissions in the Renewable Energy Directive.

d) European Commission, Renewable Energy Directive (Indirect land use is not included) for rape seed biodiesel typical greenhouse gas emissions savings 45% (typical implies an estimate of the representative greenhouse gas emission saving for a particular biofuel production pathway) and default greenhouse gas emissions savings 38% (default implies a value derived from a typical value by the application of predetermined factors and that may, in circumstances specified in this Directive, be used in place of an actual value.

e) Rapeseed oil forms the major feedstock in the EU and accounts for two thirds of total input in biodiesel production.

f) After years of rapid use increases, EU-27 biodiesel consumption seems to have reached a plateau. In 2011, Germany, France, Spain, Italy, and the UK were the largest biodiesel consumers in the EU. For 2012, EU consumption is forecast to marginally increase by 0.4%, driven almost exclusively by MS mandates and to a lesser extent by tax incentives. Increases are projected, most prominently, in Poland, France, and the Benelux. For 2013, EU-27 consumption is forecast to marginally decline as projected increase in Romania, Poland, and Ireland are more than offset by an expected reduction in Germany.

g) There are necessary the studies for using realistic environmental and occupational exposures from new technology diesel engines including low sulfur fuels and exhaust after-treatment.

h) In fact, during recent years strong efforts were made to minimize diesel engine emissions-related health hazards.

i) Although, diesel engine emissions exposures in developed countries changed strongly during recent years, reliable animal experiments or epidemio-logical studies concerning the use of new fuels and technologies are almost lacking.

j) The use of blends with content up to 5% biodiesel has no significant impact on the emissions and their toxicity. An increased mutagenicity was observed with blends containing 20%. Nevertheless, increased mutagenic effects were observed under specific conditions. Accordingly, the problem concerning blends of diesel fuel with biodiesel (B20) should be investigated with high priority.

k) No comprehensive risk assessment for diesel engine emissions from biodiesel and its blends is possible In regard to a comprehensive hazard characterization it is urged to develop a panel of standardized and internationally accepted protocols which allow a reliable assessment of possible health hazards which may arise from the combustion of new fuels compared to conventional diesel fuel. These methods should be robust and should reflect the various health hazards associated with diesel engine emissions to supplement data on regulated emissions. Methods for the generation of the exhaust and sample preparation should be harmonized.

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