

Project No. 4. Innovative technologies for hydrogen and bio-fuel production, storage, quality control, quality sustainment and use in Latvia

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Tasks

1. To work out the improved methods for biodiesel production process and to clarify the regularities for the changes of the mixed diesel fuel characteristics when the amount of bio-diesel in the mixed fuels has been increased. To work out the proposals for the development of biodiesel production and mixed diesel fuel storage, quality control, quality providing and use of the diesel fuels. It is planned to investigate the opportunities to improve the production process by changing the reaction parameters and catalysts, to obtain biodiesel with the higher quality in a technologically simple way. The investigations of the improvements of the industrial process of biodiesel production are planned also in field of by-product. Development of the selective oxidation methods of the biodiesel by-product – glycerine, to obtain expensive market products and thus to decrease the costs of bio-diesel fuel production are planned. This challenge is to be realized with the use of original transition metal catalysts.

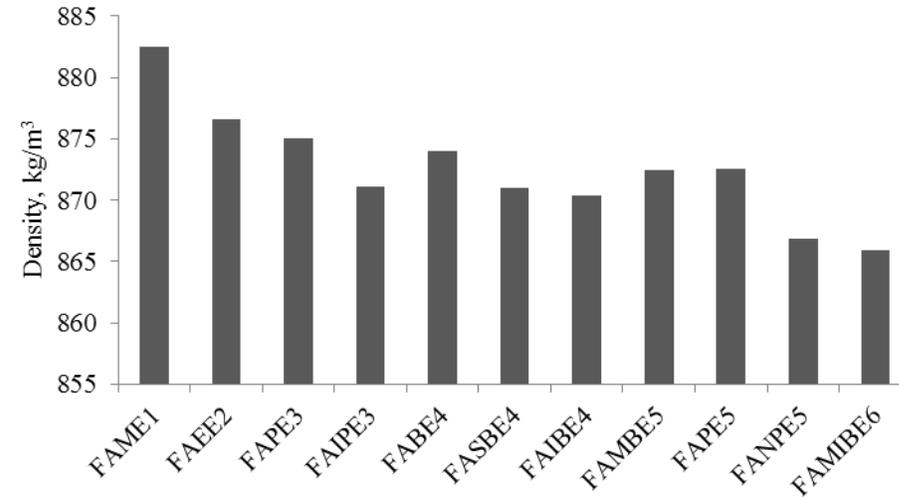
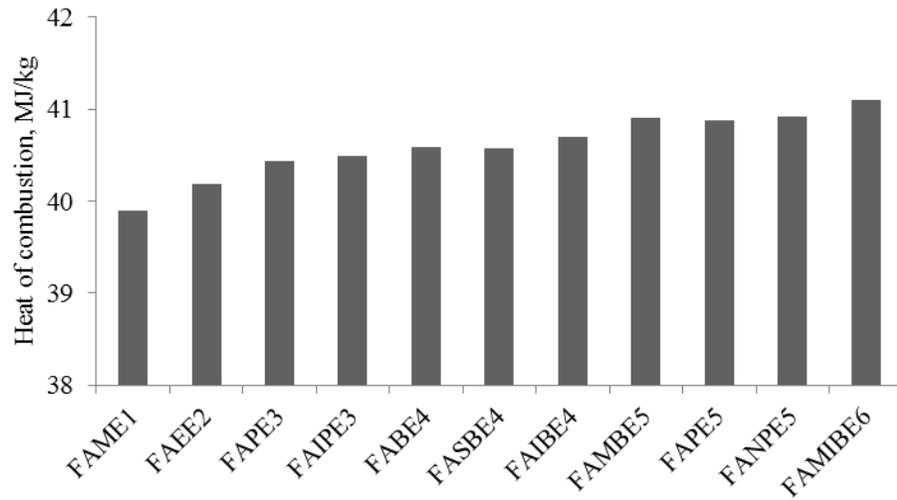
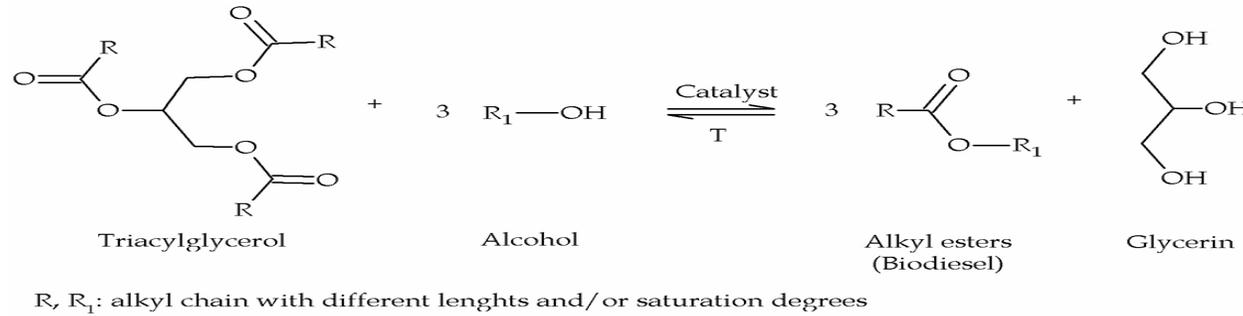
2. To work out the innovative catalytic thermal conversion technologies for obtaining qualitative bio-oil .

The industrial biomass that is not useful in food industry (plants for energy obtaining, agricultural and forestry wastes, carbon containing industrial, manufacturing and municipal wastes) is considered to be the raw material for the future biofuels, but the lack of the corresponding technologies prevents the commercial use of it. The challenge is the development of the technologies for obtaining the high quality bio-oil from lignocellulose materials (wood, straw) by the use of the newest thermochemical methods for biomass conversion - catalytic pyrolysis and catalytic hydrothermal and solvothermal liquefaction. Despite the differences of the mentioned above methods for the conversion of biomass, in both ways it had been obtained three different products – non-condensable gases, bio-oil and char. The content of each product as well as the quality of bio-oil is dramatically influenced by the conditions of the proceses (the reglament for the temperature, atmosphere, pressure) and the catalyst. The systematic labour and time consuming investigations will be done to provide the realization of the challenges of the Project with the use of cheap metal oxide catalysts, commercial hydrogenation catalysts and the original transition metal and noble metal supported nanocatalysts.

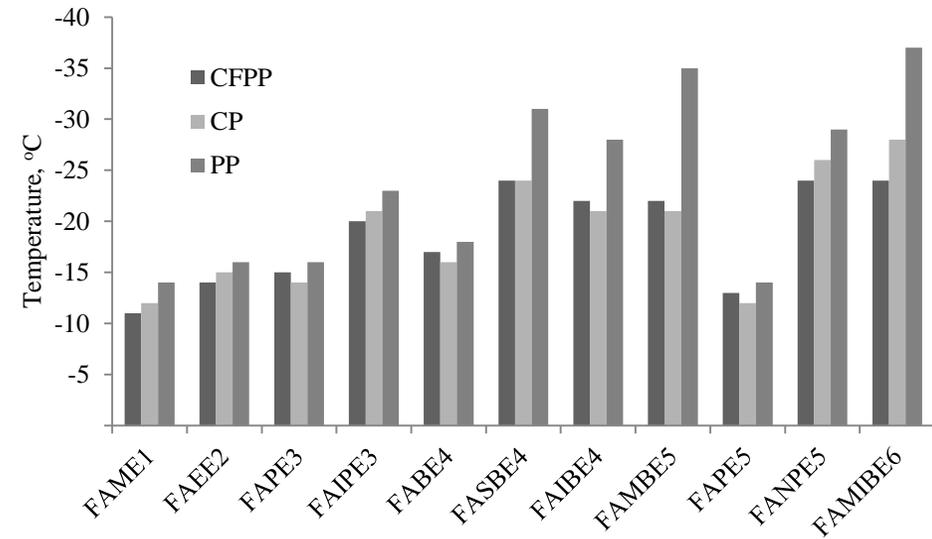
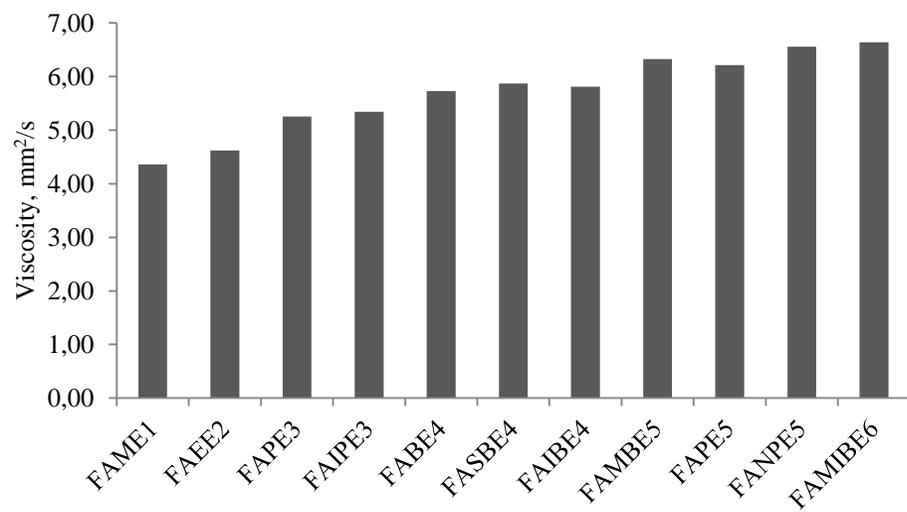
3. To be involved in the education process the possibilities for students to have practice and the eventual work accordingly the employment market demand. All the working groups do provide the possibilities to work out the qualification and promotion works, and in practice the students of RTU would be the most interested in this.

1.Improved methods for biodiesel production process

1.1. Improvement the properties of rapeseed oil biodiesel using different alcohols



FAME1 R_1 =methyl; FAME2 R_2 =ethyl; FAPE3 R_3 =1-propyl; FAIPE3 R_1 =2-prpyl; FABE4 R_1 =1-butyl; FASBE4 R_1 = 2-butyl; FAIBE4 R_1 = 2-(2-methylprpyl); FAMBE5 R_1 =1-(2-methylbutyl); FAPE5 R_1 =1-amyl; FANPE5 R_1 =1-(2,2-dimethylpropyl); FAMIBE6 R_1 =4-(4-methylpentyl)



Carbon residue of distilled FFAE met the requirements of USA biodiesel standard ASTM D6751. Flash point of FFAE also complied with the requirements of EN 14214 standard which proves that FFAE do not contain volatile impurities that may affect fuel properties. It was also observed that heat of combustion and viscosity increases and the density decreases with the increase of hydrocarbon chain length in FFAE alcohol moiety. Density of all obtained FFAE corresponded to EN 14214 standard. Only FAME1 and FAEE2 met the requirements for viscosity. Increase of hydrocarbon chain length in FFAE alcohol moiety improved the cold flow properties. Derived from linear alcohols FABE4 reached the lowest CFPP (17 C), CP (16 C) and PP (18 C). CFPP, CP and PP values increased when the length of linear hydrocarbon chain contained more than 5 carbon atoms. CFPP, CP and PP values for FFAE derived from the branched alcohols are significantly lower than for those derived from linear. The lowest CFPP values (24 C) have been obtained for FASBE4, FANPE5 and FAMIBE6. Vacuum distillation helped reduce CP of FFAE closer to CFPP value. The main factor that affects CFPP results (standard DIN EN 116) at lower temperatures is rapid increase of viscosity, therefore in individual cases CP values of FFAE are lower than CFPP.

K.Malins, V.Kampars, R.Kampare, J.Prilucka, J.Brinks, R.Murnieks, L.Apseniece. [Properties of rapeseed oil fatty acid alkyl esters derived from different alcohols](#). Fuel, Volume 137, 2014, 28-35. (IF = 4.186, SNIP 2,568).

1.2. Elaboration of heterogeneous catalyst for biodiesel synthesis from cheap resources



Invention allows to use fatty acids or oil with high fatty acid content for the synthesis of high quality biodiesel fuel for transport. The new solid catalyst has a high activity (at least by 40% higher than known) and can be easily regenerated for the repeat use. The sulfonated carbon based catalyst can be utilized also for pretreatment of low quality oils. The catalysts could be used to convert free fatty acids (FFA) present in acid oils into corresponding methyl esters at low temperature. The esterification activity was found to be dependent on the initial FFA concentration found in the acid oil as well as methanol-to-oil molar ratio. The two step synthesis of biodiesel by use the new catalyst for industrial production has been recommended.

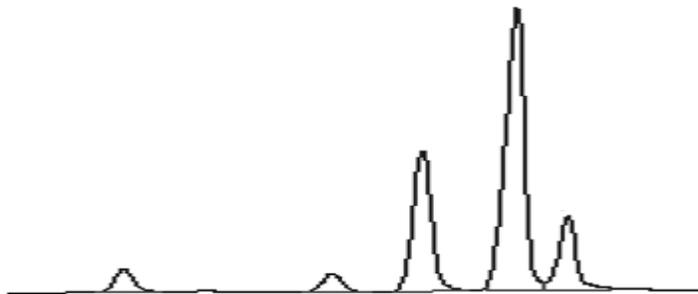
J.Brinks. K.Malins. V.Kampars. **Synthesis of sulfonated carbon based catalyst for biodiesel production and its use**
Latvian patent, 2014, Nr. P-14-15.

1.3. Control of the by-product glycerol yield and glycerol valorization

1.3.1. Control of interesterification process by GC

Improving the biodiesel production process was tempted by the interesterification with methyl or ethyl acetates. FAME (FAEE) and triacetin (glycerol triacetate, TAG) are the main products in this process. In interesterification process, sodium methoxide solution in methanol as catalyst can be used. Then the reaction outcome contains a mixture of products: the ones from triglyceride interesterification and triglyceride transesterification. In side reaction TAG could react with methanol, forming DAG (diacetin, both isomers), MAG (monoacetin, both isomers) and G (glycerol). For effective use, the reaction mixture should be analyzed and separated into the components.

A convenient method for the analysis of commercial acetylated glycerol samples based on ^{13}C NMR is presented with the accuracy comparable to the standard gas chromatographical approaches. The advantage of method is that it does not need any sample derivatization procedure by silyl groups and its application is much more straightforward, as compared to the published ^1H NMR analytical procedure.

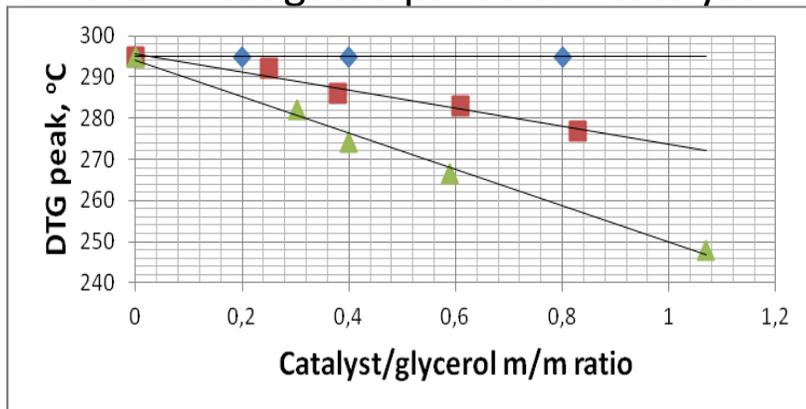


Chromatogram obtained with DB5HT column for commercial acetylated glycerol sample quantification

Z.Sustere, R.Kampare, E.Liepins, V.Kampars. The composition of commercial acetylated glycerol samples determined by ^{13}C and ^1H NMR. The comparison with gas chromatography. *J.Analytical Chemistry (Russia, N10809)*.**2014**, 69(8) 838–843. *IF=0.812*

1.3.2. Thermal decomposition of glycerol

In order to elaborate a simple method for the comparison of catalyst activity in the reactions of thermal decomposition of glycerol, thermogravimetric analysis (TGA) of glycerol and its mixtures with catalysts Pt/C and Pd/Al₂O₃, supports of catalysts and sand were conducted at different heating rates under nitrogen atmosphere. By the use of temperature profile: ramping to the isotherm 100 °C at heating rate 50 °C/min, 5 min for soak segment and linear heating in the temperature range 100 – 350 °C at the heating rate 50 °C/min the water evaporation stage is excluded and the mass loss curve is relative simple with a characteristic peak of the derivative curve (DTG). The DTG peak values are not influenced by sand and supports of catalysts, but linear dependent on the catalyst/glycerol mass ratio. The slope of this linear correlation for 5% Pt/C is twice larger than the slope of linear correlation for 3,19% Pd/Al₂O₃, from where we concluded that the investigated platinum catalyst is twice more active in the thermal decomposition reaction of glycerol than the investigated palladium catalyst.



DTG peak values versus catalyst/glycerol mass ratio x - sand, G - 3.19% Pd/Al₂O₃, Δ - 5% Pt/C.

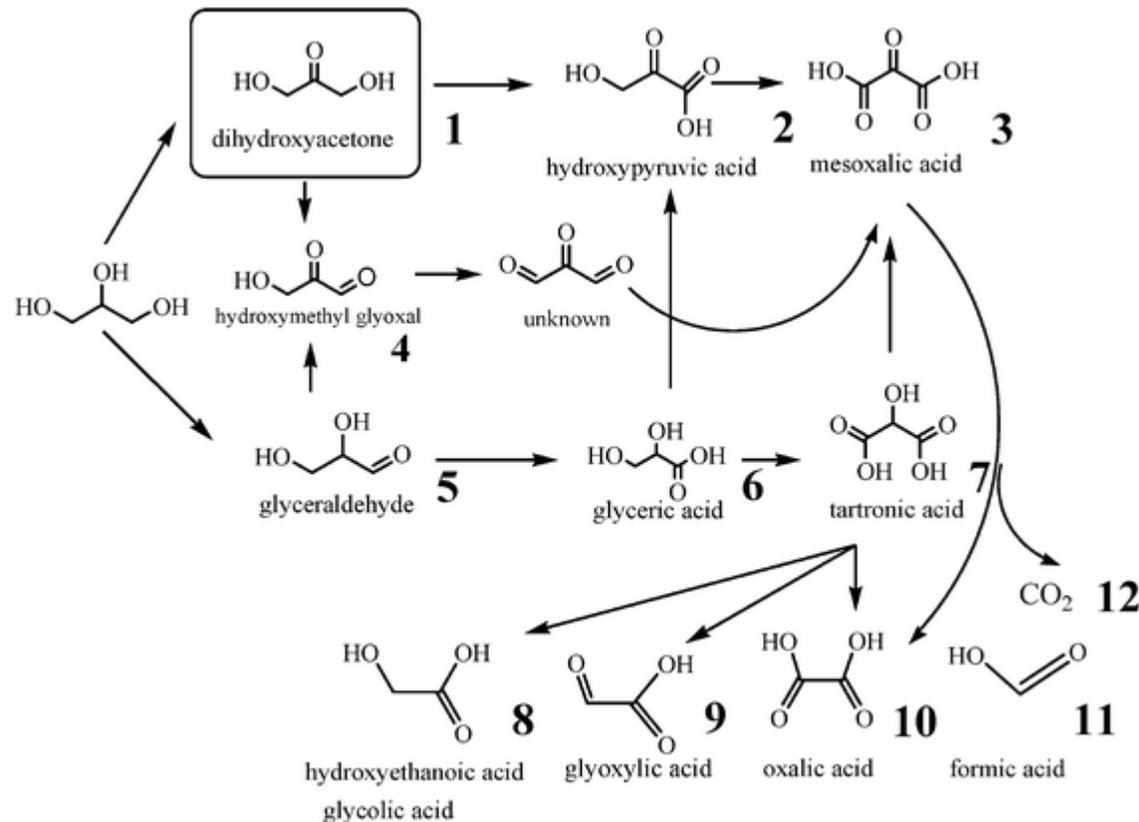
V.Kampars, K.Lazdoviča, R.Kampare. THERMOGRAVIMETRIC COMPARISON OF CATALYTIC ACTIVITY OF Pt/C and Pd/Al₂O₃ in the thermal decomposition reaction of glycerol.

Proceedings of 22nd European Biomass Conference and Exhibition Proceedings of 22nd European Biomass Conference and Exhibition, Hamburg, 2014, EU BC&E 2014 Online Conference Proceedings, DOI code,

<http://www.etaflorence.it/proceedings>, 1140-1046

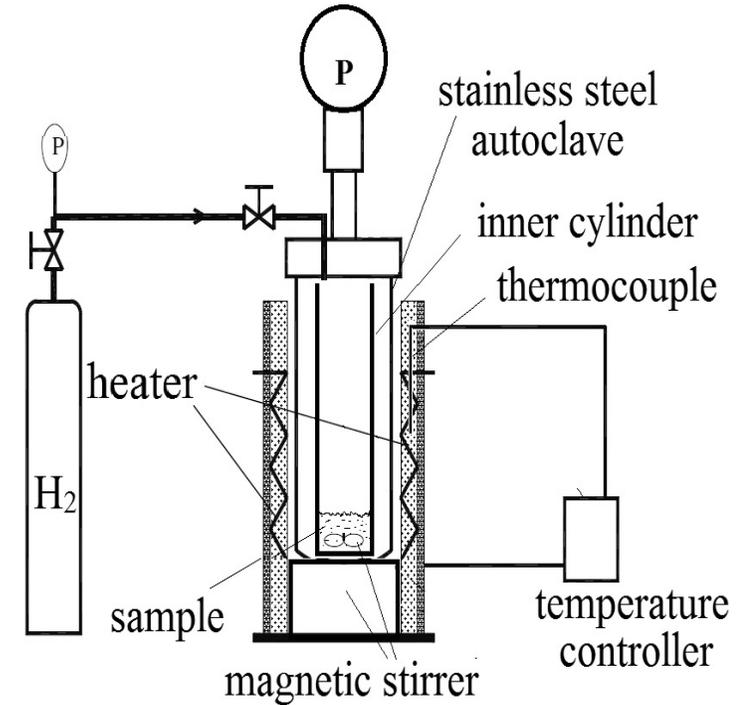
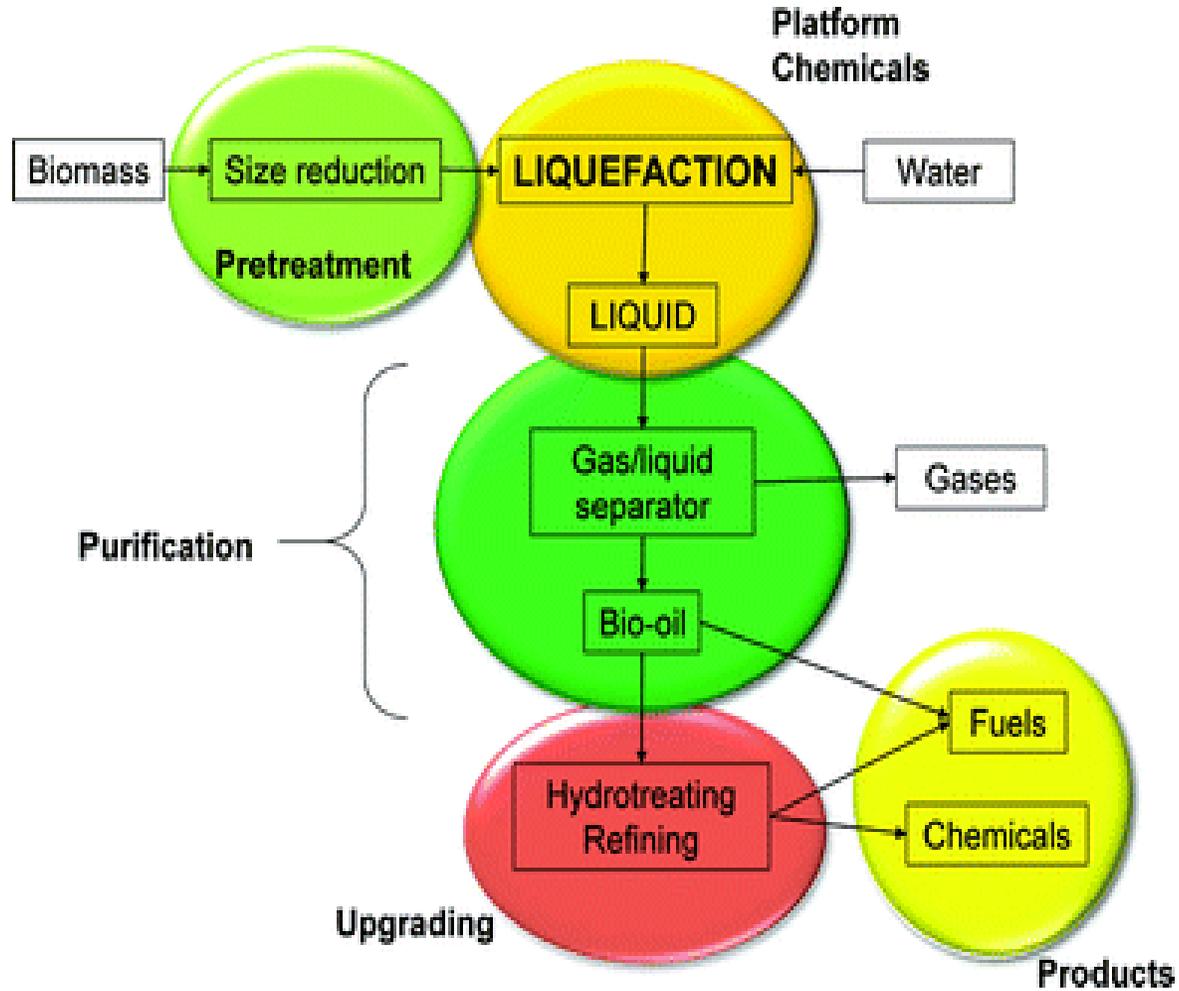
1.3.3. Synthesis of glyceraldehyde by selective oxidation of glycerol

Several novel monometallic platinum catalysts supported on metal oxides (Al_2O_3 , Y_2O_3 , $\gamma\text{-Al}_2\text{O}_3$, Lu_2O_3 , $\text{ZrO}_2\text{-Y}_2\text{O}_3$, TiO_2 , SiO_2 , $\gamma\text{-AlO}(\text{OH})$) and activated carbon (C) were synthesized by extractive-pyrolytic method and tested in glycerol oxidation processes without base addition to obtain glyceraldehyde. It was found that Pt catalyst activity is strongly influenced by support nature, oxygen partial pressure and Pt loading. Pt/ Al_2O_3 and Pt/ SiO_2 catalysts exhibited the highest activity but their selectivity to glyceraldehyde significantly decreased when glycerol conversion increased.

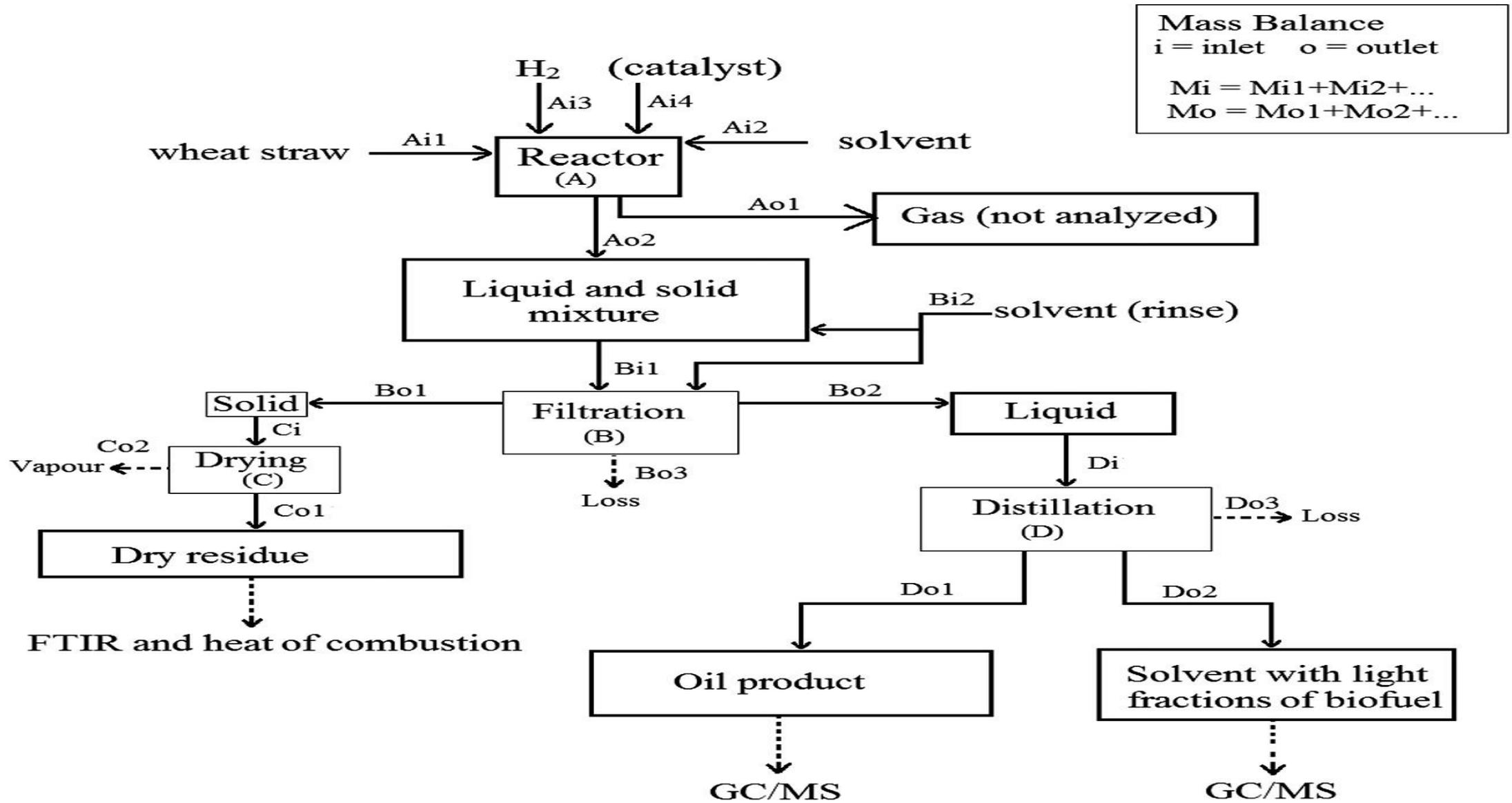


S.Chornaja, E.Sproge, K.Dubencovs, L.Kulikova, V.Serga, A.Cvetkovs, V.Kampars. Selective oxidation of glycerol to glyceraldehyde over novel monometallic platinum catalysts. Key Engineering Materials, Vol. 604 (2014), pp 138-141. IF0.21

2. Synthesis of bio-oil by solvoliquefaction of wheat straw



The experiments were performed in a 100 mL batch reactor under hydrogen pressure of 70 bar.



During solvothermal liquefaction, biomass can be partially or completely dissolved in an appropriate organic solvent at moderate temperature (120–400 C). Partial solvolysis of biomass provides valuable chemicals mainly pure cellulose and phenolic compounds, while complete solvolysis provides fuels. Different organic solvents such as polyhydric alcohols, phenol, ethylene carbonate, dioxane, ethanol, acetone, supercritical phenol and supercritical alcohols have been used in liquefaction process. In this work wheat straw was hydroliquefied in presence of **catalyst 66%Ni/SiO₂–Al₂O₃** at a temperature of 300 C for 4 h in ethanol or toluene in order to obtain bio-components which are useful for fuel purposes.

The main compounds of the oil produced during the liquefaction of hemicellulose, cellulose and lignin of wheat straw in both solvents are: **tetrahydrofuran-2-methanol, 1,2-butanediol and butyrolactone.**

Besides the mentioned compounds, **ethanol** favoured the decomposition of bigger molecules to short-chain alcohols such as 1-butanol, 1,2-propanediol and 1,2-ethanediol.

Toluene contributes to the production of furans and other cyclic compounds. The light fractions distilled together with the solvent also contain the following: 1-propanol, 2-methyl-cyclopentanone, acetic acid and ethyl acetate.

R. Murnieks, V. Kampars, K. Malins, L. Apseniece. Hydrotreating of wheat straw in toluene and ethanol, *Bioresource technology*, 2014, 163, p.106–111. (IF = 5,6, SNIP 2,463).

3. Education process

Institute of Applied Chemistry is involved in the education process (realisation of study programs «Chemistry» and «Chemical Technology») and offers the possibilities for students to have practice and the eventual work accordingly the employment market demand. Institute provide the possibilities to work out the qualification and promotion works, and 4 master thesis during the 2014. year under the guidance of the institute were defended.