Synthesis of Fuels from Biomass Derived Oxygenates

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Acknowledgment

Abstract

Direct conversion of wooden biomass to liquid fuels is performed in two-step process. First step is to transform cellulose, hemicelluloses and lignin into to basic chemical compounds which they are assembled of (mainly basic sugars, cyclic C_6 and C_5 oxygenated hydrocarbons). These compounds are then further transformed to polyethylene glycol and polypropylene glycol.

Nevertheless, this project is focuses on testing of catalysts for second step, which is transformation of obtained C_2 and C_3 polyalcohols to C_{6+} hydrocarbons (diesel-like compounds) with concurrent reduction of oxygen content. Produced liquid is then suitable for combustion in car engines.

Most important chemical reaction for this process is aldol condensation. Aldol condensation is complex, little explored reaction, which behaves differently according to reactants present in the process. Better understanding of such reaction and its followed application in second step direct catalytic biofuel production was done by preparation and testing of various types of catalysts and theirs properties.

Preface

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

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1 Introduction

Increasing energy consumption[1], constant rising price of energy and especially volatility of crude oil on the market with current decreasing reserves of fossil fuels, dependency on oil exporting countries but mainly environmental concerns for rising green house gases (GHG) in the atmosphere and global warming lead to look for new solution and paths how to produce sustainable renewable energy resources. These reasons are the most important driving forces in development source of energy available anywhere in the world. Crude oil is key and hardly replaceable resource across the globe, unfortunately among all the oil-producing countries are also often politically unstable or otherwise unreliable countries. The vast majority of transportation either public or industrial is based on combustion engines and most of those engines burn liquid fuels. To reduce dependence on crude oil without drastically change the current automobile infrastructure, beginning with combustion engines technologies and end with gas stations network. The least harmless solution is to replace nowadays-fossil liquid fuels with biofuels. Positive stances to research and development, supporting policies, and regulatory frameworks of biofuels from many countries help to rapid expansion of large-scale production. Even big players among oil production companies are showing visionary attitude by opening biofuels divisions or by financially supporting research and development at universities as cooperation of Statoil and NTNU.

Various approaches (e.g., pyrolisis, fermentation, gasification, and direct catalytic conversion) and feedstock (e.g., colza, corn, sugarcane, palm oil, jatropha, algae, and especially wooden biomass) are subject of study. Among largest producers in the world are U.S., Brazil, some European Union countries, China, and India, lately also countries from Asia-Pacific region which show great potential in future production due to easy excess to biofuel producing corpses which are specific for this geographical location and favorable climate.

R&D is moving towards next generation of biofuels, including the second and third generation of biofuels to prevent competition between biofuel production and agricultural production of corpses for food market. Algae and wooden biomass are therefore considered as major feedstock suitable for this industry. Scientists are working on solving challenges connected to processing of such feedstock i.e., main task

is to convert woody biomass which is comprised of cellulose, hemicelluloses and lignin into the sugar molecule. They use a many different techniques to achieve it. Biological or catalytic conversion of cellulose to sugars is considered as two main pathways. Biological involve coupling of molecular bonds using enzymes, fungi, and microbes while direct catalytic route transform biomass to fuels in two main steps but more about it later in this project. Despite significant support from the governments and companies and great effort of researchers, commercial development of next biofuel generation is not expected to be realized in 10 years horizon.

Nevertheless, biofuel industry is booming. Global production of biofuels nearly tripled since the year 2000. Global Industry Analyst goes even farther when forecast that consumption of bioethanol and biodiesel will be 135 billion gallons by the year 2018.

Note: FSU= Former Soviet Union.

Source: IEA, 2010c.
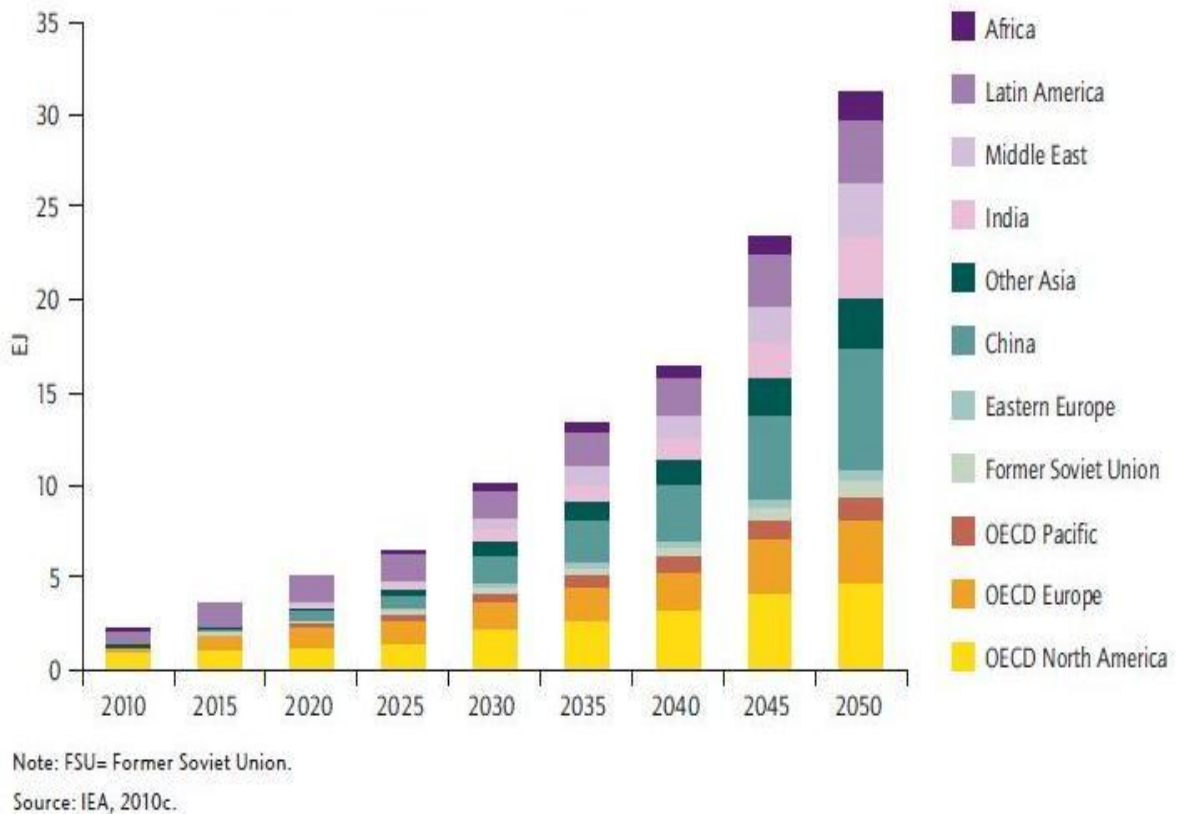
Figure 1 - Biofuel demand by region 2010 – 2050 [2].

2 Literature part

Crucial is to move from production of biofuels fuels (BF) form sugarcane, colza, corn etc., to second and third generation of biofuels, because of increasing concerns for food production sustainability. First generation of BF producing corps diverts away agriculture commodities from the animal and human food chain. Moreover creating of new plantations for such corps destroys the ecosystems and natural biodiversity. Finding solutions for conversion of wood and algae into liquid fuel is therefore essential to prevent such devastation and threat what represent first generation corps. Nowadays especially in Europe biggest threat for BF development lays however in economical crisis. Nobody can accurately predict what impact it would have on BF demand and future progress.

Use of biomass will help to reduce amount of produced greenhouse gases because unlike processing of fossil fuels with their subsequent conversion into the energy, significant amount of carbon dioxide is consumed for new biomass re-growth. Carbon dioxide cycle is shown on Figure 2 [3].
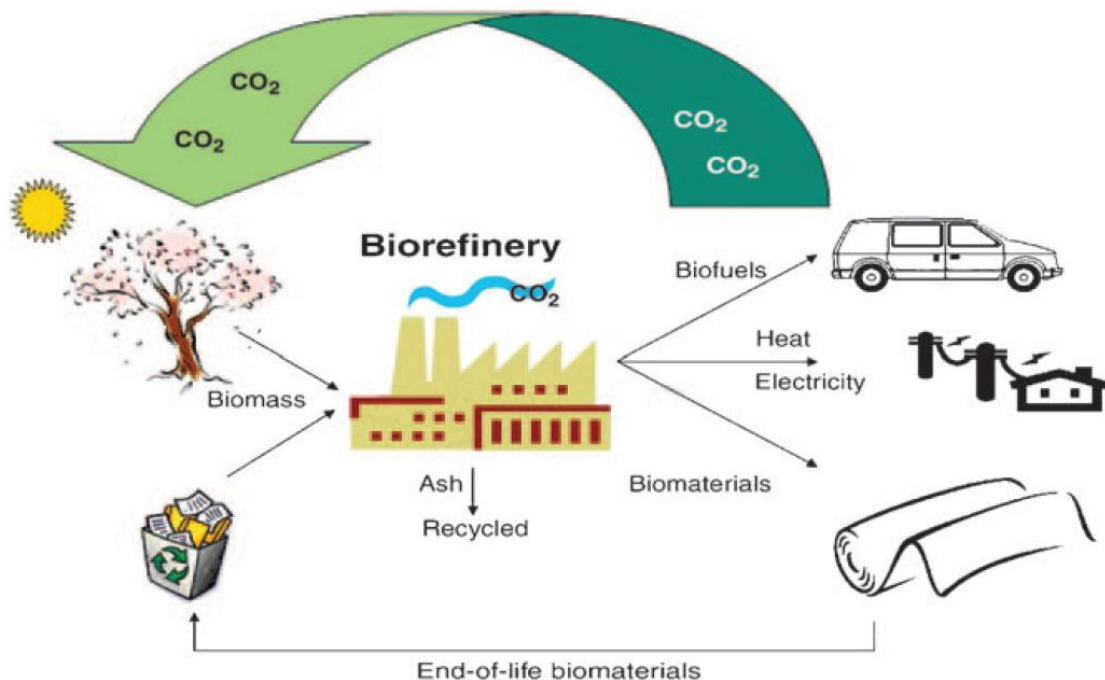
Figure 2 – Sustainable technology in an integrated biorefinery [4].

Most useful alternative to fossil fuels which is attracting more attention every day is most abundant source of biomass – cellulose [5-9]. This energy source with high potential is being currently explored.

Wood base recourses and corps were used for production of various types of products such as solvents, dyes, and fibres in the beginning of the last century [10]. Big turnover came after Second World War when all this biomass-based products were replaced by crude oil upgrades. Another milestone in production of biomass-based products was in 1970s after oil crisis when oil prices were drastically increased. These efforts unfortunately past as the crude oil price was reduced [4].

Agriculture, forestry or industry recourses are nowadays used to produce various types of energy products, fuels, and chemicals as it is summarized in Table 1. Different processes such as mechanical treatment, biological, thermal and/or chemical conversion are used for preparation of solid, liquid, gaseous fuels or/and valuable chemicals [4].

Table 1 - Renewable energy versus fossil-based energy: from multiple biomass resources to fuels and energy products [11].

Biomass production	Biomass processing	Biomass fuels	Biomass conversion
Forestry	*Mechanical*	*Solid Fuels*	*Heat*
–thinning	–chipping	–pellets	–single stove
–residues	–cleaving	–charcoal	–central heating
	–pelleting		–heating plant
Agriculture	–pressing	*Gaseous Fuels*	
–grain		–biogas	*Electricity and Heat*
–straws	*Thermal/Chemical*	–wood gas	
–manures	–drying	–hydrogen	*Central Heating*
–energy wood	–gasification		*Plant (CHP) with*
–oil plants	–pyrolysis	*Liquid Fuels*	–steam turbine
	–esterification	–ethanol	and/or
Trade and Industry		–methanol	–gas turbine
–sawn industry residue	*Biological*	–Fischer–Tropsch	–Stirling motor
–wood industry residue	–alcohol fermentation	liquids	–combustion engine
–used wood	–methane fermentation	–oil from plants	–fuel cell
–organic residue		–oil from pyrolysis	
		–esters	

According to Kyto protocol from United Nation's climate panel, biofuels either liquid or gaseous has neutral carbon dioxide balance which means that amount of emission of carbon dioxide is not larger than amount of carbon dioxide consumed by photo catalysis. More efforts need to be focused towards biofuels in order to prevent global warming which is consequence of increased amount of greenhouse gases due to use of fossil fuels [11].

First generation of biofuels produced from carbohydrates rich plants (i.e. sugarcane, starch) are notoriously know in production of biofuels – bioethanol but also for production of gaseous products, as biogas and hydrogen. Most usual way to process such plants is fermentation and hydrolysis which however is energy demanding and complex process [11].

True potential of biomass however lies in the next generations of biofuels, especially in utilization of wooden biomass. Mankind is still in the beginning of developing technologies which would be able to process wooden biomass into the biofuels and therefore no significant commercial process has been introduced so far [11].

On the other hand, well know technologies e.g. gasification process where syngas is generated can be also utilizes for biomass. Syngas, which is mixture of CO and H_2, could be further transferred into liquids in Fischer-Tropsh process BTL (biomass to liquid) or syngas could be used as intermediate in production of methanol. From BTL process olefins and/or gasoline is produced [11].

Fast pyrolysis is another way to convert lignocellulosic biomass into bio-oil. There are two possible ways how to utilize bio-oils, first is via separation where phenolic compounds and/or carbohydrate fraction are obtained and second route is via gasification of bio-oils to syngas, which is further used as intermediate in processes like Fischer-Tropsch or methanol production. Phenolic compounds could be transformed into phenolic resins and from carbohydrate fractions hydrogen can be obtained via catalytic transformation [12]. Mover heat and electricity could be generated from bio-oil as it is suggested on following Figure 3.
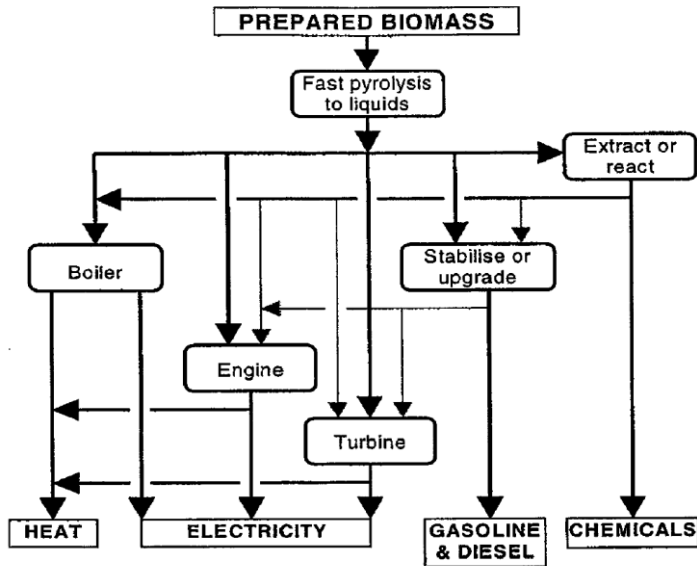
Figure 3 - Application of bio-oil [11].

High quality bio-oil could be also upgraded using FCC or hydro treating (HT), processes well know from oil refineries. Amount of fossil based energy sources could be significantly reduced if bio-oil together with hydrocarbon fractions are used as feedstock in these processes. This should be primary aim of every "green" thinking governments. Bio-oil should be introduced as co-feedstock in a conventional refinery this would greatly increase importance use of bio-oil produced from wooden biomass [10].

Overall scheme of modern biorefineries, both first and second generation are shown on following picture.
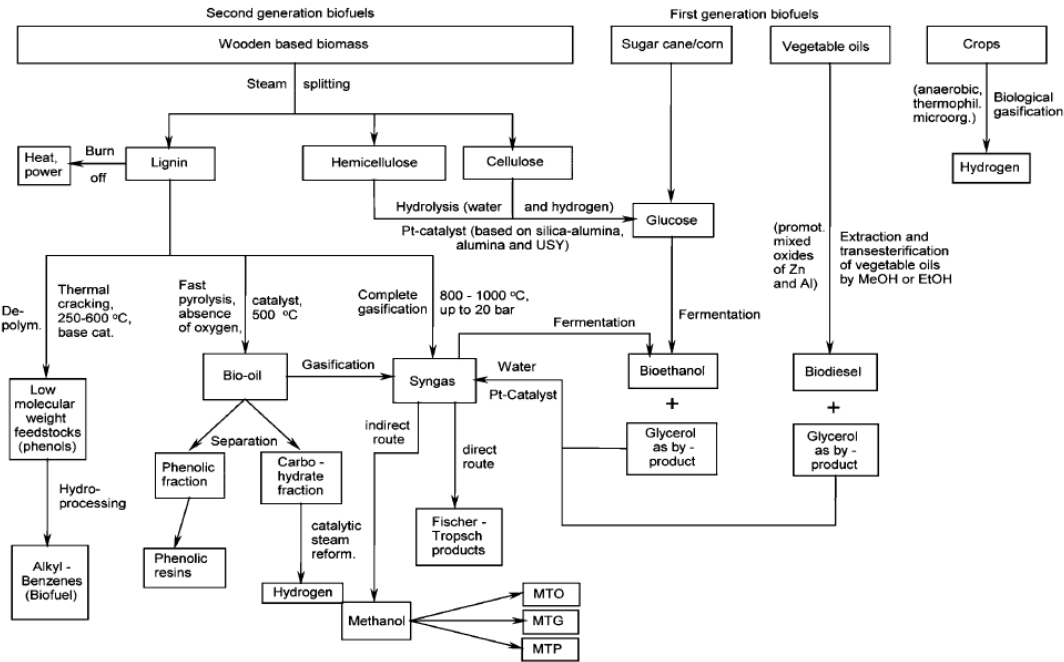
Figure 4 - Process flow in a modern wood-based biomass biorefinery. MTO: conversion of methanol into olefins, MTG: production of gasoline form methanol, MTP: formation of propene from methanol [11].

Form the scheme above it is obvious that processing of hemicelullose and cellulose could have similar patterns as first generation biomass. Via hydrolysis, these components could be transformed to simple sugars and subsequently fermented into the alcohols. Lignin via various approaches could be transformed to transportation fuels and valuable chemicals [11].

Modern bio-refinery could be compared to crude oil refinery. Feedstock is mainly cellulose, hemicellulose and lignin, which are all renewable material. Through several upgrading processes this raw feedstock is converted into valuable chemicals, fuels, heat and electricity [11].

Probably biggest complications in production of "green" chemicals are problems with logistics because to run economically efficient process, refinery needs sustainable and large supply of biomass and transporting large amounts of biomass from distant places could reverse economically profitable business to great failure. One possible solution could lie in use of microreactors, which are under development in this moment. Microreactors are much smaller, compact and easier to maintain compare to nowadays used reactors. If development of these reactors will continue and if the major parts of biorafinery could be dissembled, after all biomass in economically sustainable radius is harvested and reassembled in some other place again, it could completely change oil market. However these are only hypothetical considerations many efforts still need to be made in this particular field.

2.1   Future

Prospectively use of renewable biomass, which does not burden atmosphere with greenhouse gases, is going to be essential alternative for fossil-based fuels. Unfortunately production of biomass needs to deal with major economical obstacles, which holding back boom of this promising industry [11]:

- *"High investment costs*
- *Low volumetric energy density of biomass*
- *Lack of infrastructure*
- *Limitation to the productivity of photosynthesis*
- *Availability of cultivable land areas for the production of bioenergy plants, which are in competition with food production."*

Adopted from [11].

Probably biggest obstacle in utilization of wooden biomass into the biofuels is its low energy density. Especially low density and complicated structure of lignocellulose makes it very difficult to convert it to liquid fuels. At this moment, only catalyzed fast pyrolysis process is considered as possibility for industrial use, although to convert lignocellulose into high-quality bio-oils is still challenging and scientists are still trying to find the ways how to improve catalysts for this purpose. They believe, once high quality bio-oil is achieved it could be co-fed to standard refinery and by subsequent processes like FCC or hydrotreating converted into high quality liquid fuels [13].

There are many ways how to utilize biomass and there are various types of biomass. However, we believe that our approach, the direct conversion of wooden biomass to biodiesel, is one of the most promising methods in entire biofuels industry. A lot of work needs to be done in research, e.a. understanding of chemical reactions and theirs detail description, development of new type of catalyst which will be specially tailored for this purpose and description of its properties, e.a. basicity, acidity, active metal (if any), catalyst support, catalyst stability and its resistance towards deactivation. Least but not last is to find reaction conditions of the process and how process will be affected if it will be scaled up to industrial scale. Aim here is not find process which should be necessarily competitive to crude oil industry rather something which could coexists with it and in case unexpected events occur, cover incurred problems.

Mainly finding of different pathways of conversion cellulose into more valuable chemical compounds is being focused on. Special efforts are put into finding the pathways of conversion of cellulose into the polyols, because of wide application of these chemicals, which could be either used directly or as precursors in variety chemical processes as precursor i.e. value-added compounds and fuel synthesis [3, 14-17].

What are the main components of lignocellulose? There are three main parts of lignocellulose: cellulose, hemicelullose, and lignin. Main advantage of lignocelluloses besides it helps to reduce greenhouse gasses is that it is very abundant and non-expensive material.
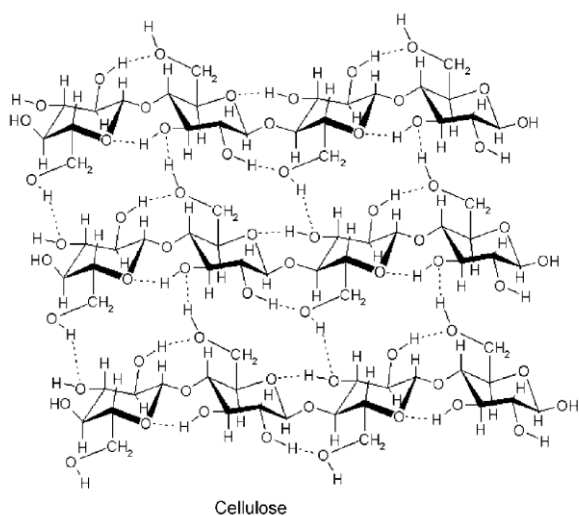
Cellulose

"Cellulose consists of linear polysaccharides in the cell walls of wood fiber, consisting of D-glucose molecules bound together by β-1,4 glycoside linkages (comprises about 41 %).

Hemicellulose is an amorphous and heterogeneous group of branched polysaccharides (copolymer of any of the monomers glucose, galactose, mannose, xylose, arabinose, and glucuronic acid); hemicellulose surrounds the cellulose fibers and is a linkage between cellulose and lignin (about 28 %).

Glucose

Galactose

Mannose

Xylose

Arabinose

Glicuronic Acid

Hemicellulose
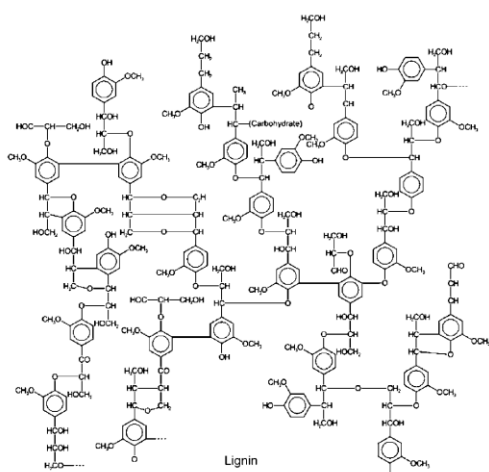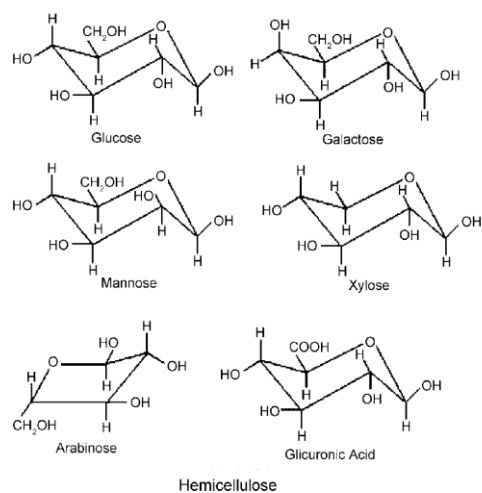
Lignin

Liginin is a highly complex three-dimensional polymer of different phenylpropane units bound together by ether and carbon-carbon bounds. Lignin is concentrated between the outer layers of the fibers of polysaccharides together (about 27 %)."
Ligunocellulose description adapted from [11].

In addition, small amounts of extraneous organic compounds are found in lignocellulosic materials (about 4 %).

To reach sorbitol and polyols as product from cellulose, hydrolysis of cellulose into glucose need to be done, this step is usually done by using strong inorganic acids as catalyst. Next step is hydrogenation of cellulose to obtain desired product [14, 18-20]. Various types of catalyst are used for this purpose (i.e. Ru/C) showed to be very efficient in combination with heteropoly acids for conversion of cellulose into hexitols (sorbitol, mannitol) [18, 19]. Another procedure is use of Pt/Al_2O_3 which does not require use of any mineral acid and conversion of cellulose into hexitols happens in water [21]. Further research of catalyst is focused mainly on Ru/C catalyst, where support is being substituted with carbon nanotubes [22] or carbon nanofibers and ruthenium is being replaced with Ni [23]. Noteworthy results were obtained by Ji et al. of conversion of cellulose to ethylene glycol over tungsten carbide catalysts ($Ni-W_2C/C$), they were able to convert up to 60 % of cellulose to ethylene glycol [24, 25]. Although reaction mechanism of this process was not fully specified, these findings open the new pathways of sustainable production of ethylene glycol

This research was moved even further by Liu et. al. [26] who presented their catalyst Ru/C in the presence of WO_3 which is able to convert cellulose into ethylene glycol, propylene glycol, or sorbitol as main product as it is shown in following Figure 5.
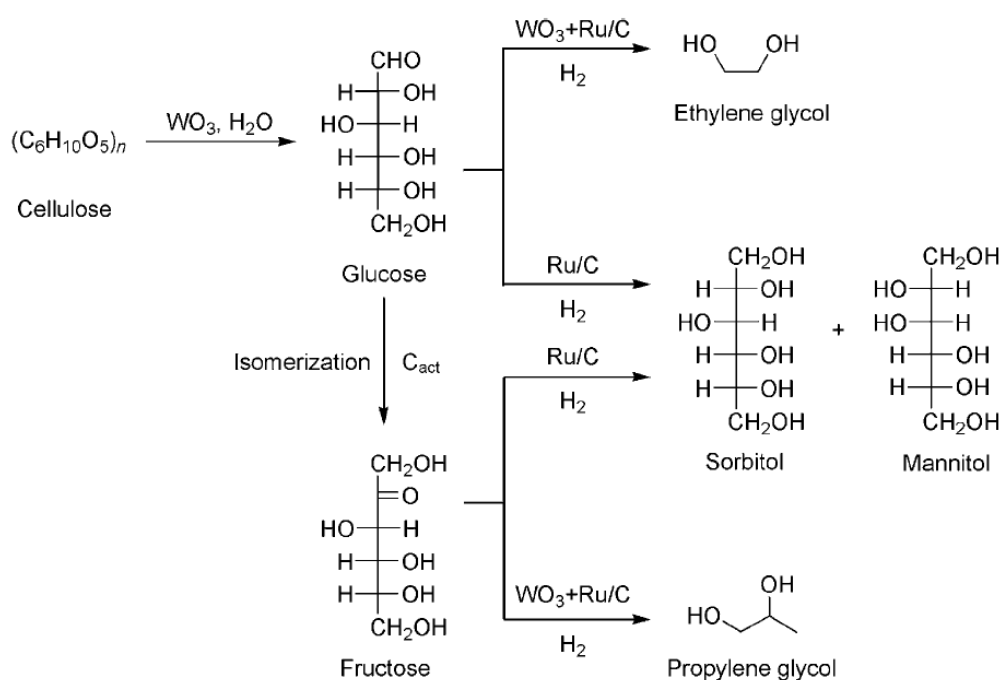
Figure 5 - conversion of cellulose into ethylen glycol, sorbitol and propylene glykol

Key component in production of propylene glycol and ethylene glycol is WO_3, which is depending on the domain size of it, can promote both, hydrolysis of cellulose and also selective coupling of C-C bonds in sugar intermediates. Liu et al. were able to obtain yield more than 30 % of propylene glycol directly from cellulose.

2.2   Chemical reactions

Direct catalytic conversion of biomass into the biofuels consists of two main steps [27,28]. First is conversion of cellulose, hemicellulose, and lignin to C_3 and C_2 polyalcohol hydrocarbons and second is upgrading of polyalcohols to C_8-C_{20} low-branched hydrocarbons with low oxygen content similar to diesel compounds. Whereas first step is not subject of this project, two key chemical reactions are necessary for second step direct catalysis of biomass into the biofuels.

2.2.1   Aldol condensation

Reaction mechanism to reduce C/O ration with current lengthen of hydrocarbon chain is called aldol condensation [27, 29, 30]. Acid and base catalysts usually catalyze aldol condensation. The fundamentals of aldol-type condensation are reaction between aldehyde and keton molecule with current dehydrogenation where water and unsaturated aldehyde is formed [31]. In research of aldol-type condensation various types of oxides were used e.g., MgO, Mg-AlO$_x$, ZnO[32, 33] or alkali metal salt on silica. Also some of the metals (Cu, Zn, Cr, Mo, W, Mn) convert at elevated temperatures around 533-573 K via Guerbet reaction primary alkanols to β-alkylated dimmers [34].

Aldol condensation reaction requires specific conditions for specific reactant meaning that reaction conditions would be different for aldol condensation of isophorone and for propylene glycol. Probably biggest difference among other will be selection of catalyst for each reaction. Crucial is then selection of proper strength of the catalyst. The first step of aldol condensation is removal of the proton from the structure looking like R_1-CH_2-R_2 where the acidity of the removed proton depends on functional groups R_1, R_2. The reason for proper selection of the strength of the base is that base needs to be strong enough to carry out the reaction but if it would be too strong it could lead to formation of byproducts or even to deactivation of the catalyst itself. Dissociation constant for aldehyde and ketone should be around 19.7-20. This is range for strong bases but not for superbases[35].

2.2.2   Ketonization

Ketonization is the process of deoxygenating of polyalcohol molecules[36]. Today aim is to minimize hydrogen feedstock, which is used in the reaction, and simultaneously minimize formation of coke, which is generated during the reaction. Amount of used hydrogen significantly influence cost of the bio-fuel generating process. Therefore, main task is to keep the consumption on the lowest possible level.

Also derivates form biomass is complex mixture of hydrocarbons with various functional groups (e.g., –OH, -C=O and –COOH) [36]. Especially carboxylic acids could cause problems to the process due to high acidity [37]. The processing equipment could suffer from corrosion, which could subsequently lead to fatal damage of the device. Also high acidity has undesirable effect on biofuels stability. High contain of acidic functional groups will enhance degradation of the product. Aim therefore is to transform all cellulose and hemicelluloses in the first step selectively to the polyalcohols to avoid all these problems.

Moreover, high content of oxygen in biomass structure needs to be taken into the account because it has high chemical reactivity at elevated temperatures. It could lead to entire natural decomposition of the reactant. Serrano-Ruiz and Dumesic claims, it is beneficial to work with biomass in aqueous solution due to its high solubility in water. They suggest the best way of biomass catalytic treatment is as aqueous solution at mild temperature programs [36].

2.3   Basicity of the catalyst

As it was mentioned above crucial is to find perfect balance between strength of acid and basic properties of the catalyst for aldol condensation, which depends on chemical compound and varies with its functional groups.

The acid-base properties of the oxides vary with adsorption ability of the ions onto their surfaces. The electric neutrality is maintained with protonation and deprotonation of hydroxyl groups, which produce electric charge. From the study of Hiroki, Noriaki, Ryusaburo it was found the intensity of cation exchange (deprotonation) increases in order: $Al_2O_3 < Fe_3O_4 < TiO_2 < MnO_2$. Protonation decreases in the same order [38].

Measuring or controlling of surface potential for the oxides is considerably difficult since all the models of electric double layer are evaluated on ideal oxides [39-42]. Ideal oxides have smooth surfaces, few pores, well defined composition and of course structure meet double layer assumption. However, natural oxides rarely meet these conditions. Even if the ideal oxides are prepared in the laboratory, it is still significantly difficult to make electrodes that could be used for measuring the surface potential.

The acid and base hydroxyl groups $-OH_{(a)}$ and $-OH_{(b)}$ exchange anion and cation as it is shown in following equation *2–I*:

2–I

$$-OH(a) + M^+ \rightleftharpoons -O^- \cdot M^+ + H^+ \qquad (1)$$

$$-OH(b) + H_2O + X^- \rightleftharpoons -OH_2^+ \cdot X^- + OH^- \qquad (2)$$
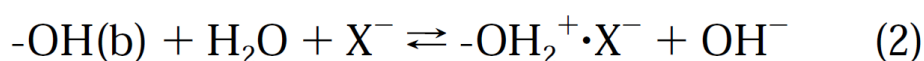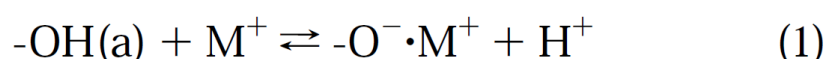
where the anions and cations are electrostatically adsorbed to the charged sites of the hydroxyl groups. This proves that solid materials can generate acidic and basic sites separately on the same surface. In addition, it shows that in homogeneous solution acid and basic sites could not coexist without interacting with each other.

One of the most accurate methods for description of acidic and basic properties of oxides is titration by gas-phase probe molecules[43] .Probe molecule for examination of acidic properties of catalyst is ammonia, and carbon dioxide is used for inspection of

basic sites. Carbon dioxide is acidic molecule, which strongly interacts with the basic sites of the oxide. In addition, CO_2 interactions with metal atoms and ions were closely studied. There are several factors influencing the acidity and basicity of the oxide, mainly it is charge, radius of metal ion[44]. Factors that influence the bond between oxygen and metal are coordination number, filling of the d-orbital, and the nature of other ligands. For basic properties of metal oxides, chemisorption of CO_2 on the metal oxides was observed as it is shown on following *Figure 6*.
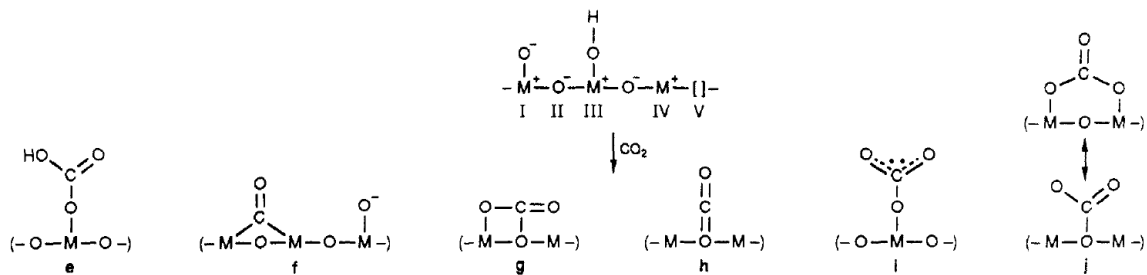
Figure 6 - e) adsorption of a hydroxyl group with formation of a superficial hydrogencarbony ion; f) adsorption on the metal cation and dissociation of the resulting bonding; g) adsorption on the metal ion and the neighboring oxygen ion and formation of a bident[43]

Appearance of bonding of carbon dioxide onto the metal oxide depends on physicochemical properties of the chosen oxides, which are influenced by preparation technique starting material, and the different pretreatment techniques. Form *Figure 6* stronger adsorption of carbon dioxide could be referred to a monodentate carbonate (i, j) and the weaker can be referred to the bidentate (e,g). Strength of adsorption of carbon dioxide to the surface suggests the strength of the oxide. The type of the bonding onto the catalyst surface could be detected form infrared spectra of chemisorbed CO_2[45]. Lanthanides and actinides (La_2O_3, Nd_2O_3, Pr_6O_{11}, ThO_2) belonging to medium and strong basic oxides[43]. Likewise, CaO, ZnO, and MgO were classified as strong basic oxides. Further bidentate species ZrO_2, TiO_2, BeO represent typical medium strength basic oxide. Alumina on the other hand represents typical amphoter due to remarkable chemical heterogeneity. Properties of alumina are strongly dependent on calcinations temperatures and the extent of hydration because in different conditions alumina could be classified as bidentate specie, so medium strong basic oxide.

Average heats of CO_2 adsorption was plotted against charge/radius ratio of the oxides as you can see on below picture[44]. General hypothesis is the greater the degree of covalency of the oxide the higher value of the charge/radius ratio. Low values of the charge/radius will make oxide more ionic and that will increase the amount of the basic sites.
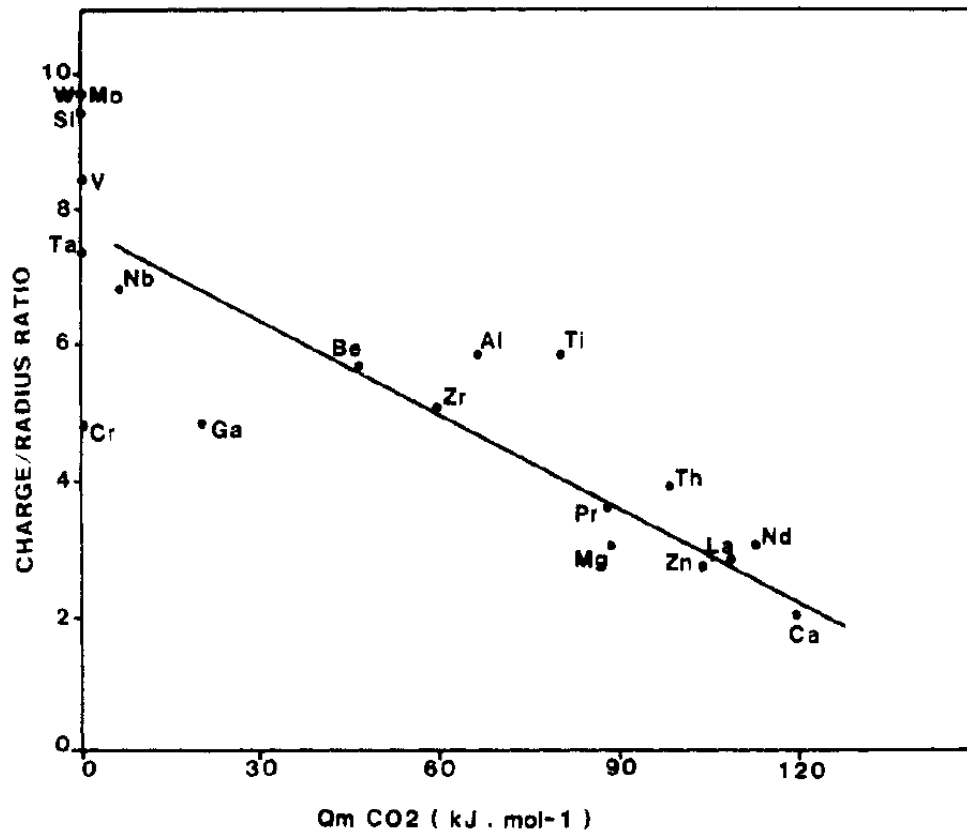
Figure 7 - Charge radius ratio as a function of average heat of CO_2 adsorption[43].

Looking on the graph acid basic properties of the oxides change form left hand side, where mainly oxides with the acidic characteristics are located to the middle part, which is occupied mainly by the amphoteric oxides to right hand side, which is reserved for the strong basic oxides.

Important aspect for the formation of the light alkanes is also acidity of the used catalyst. In some cases use of SiO_2 and Al_2O_3 as catalysts support or use minerals acids like HCl in the feed to increase acidity of the system is beneficial to increase selectivity of alkanes formation [28]. Higher acidity of the system enhances dehydration and hydrogenation reactions on the expense of hydrogenolysis and reforming reactions.

2.4   Second step in biofuels synthesis

Second step in preparation biofuels form biomass is transformation of polyalcohols to hydrocarbons. The main aim is therefore focused on removing oxygen out of polyalcohols [7, 46, 47]. Oxygen could be removed from the hydrocarbon structure as H_2O, CO, or CO_2 depending on used catalyst and reaction conditions. Therefore, several reaction mechanisms are considered. Each of them describes how the oxygen atom is released. Oxygen could be released as water through dehydration or hydrodeoxygenation [46, 48, 49] reaction. Either hydrogen is used form an external source or from reaction itself. Hydrodeoxygation takes place if hydrogen from external source is used but if the water molecule is formed from hydrogen present in the reactant molecule structure then releasing hydrogen as water is called dehydration.

Second way to eliminate oxygen is as carbon containing molecule i.e., elimination of CO from the structure of polyalcohol through decarbonylation or similarly elimination of oxygen as CO_2 via decarboxylation.

Significantly important reactions for generation of biofuell are also hydrogenolysis and hydrogenation. These reactions generate hydrogen *in situ* as water-gas shifted reaction *2–II* [50-52].

2–II

$$CO + H_2O \rightarrow CO_2 + H_2$$
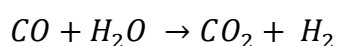
This particular reaction is highly desired for the system because it reduces hydrogen consumption form the external source that is economically beneficial due to high price of hydrogen.

Cu-based catalyst without requirement of oxide support could be used for C-C coupling monofunctional reaction. O-atoms are removed as CO_x instead of H_2O [31]. It reduces consumption of external hydrogen and working with the lower pressures decrease initial cost of processing equipment.
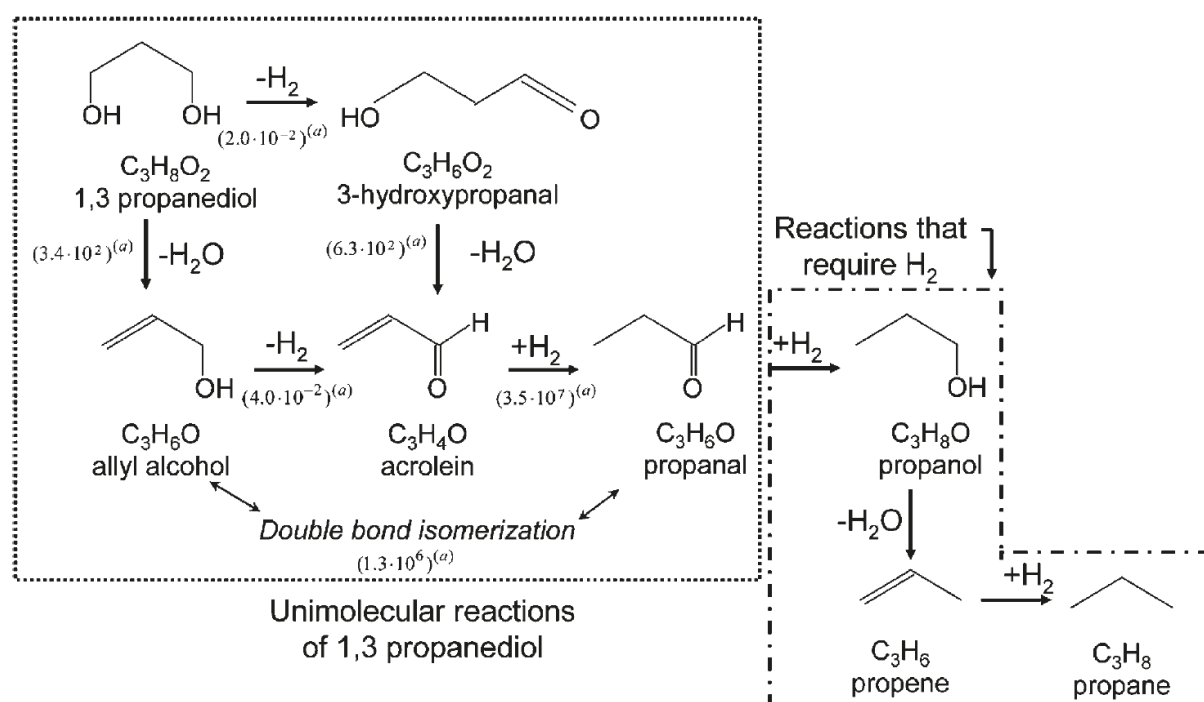
Figure 8 - Reaction Network for 1,3 - Propanediol Deoxygenation[31].

Sad, Neurock, and Iglesia also worked with $Cu/ZnO/Al_2O_3$ catalyst. Possible reaction pathways for propanediol deoxygenation are showed on *Figure 8*. Whole 1,3-propandiol was converted into propanal-propanol mixtures with traces of other products even without adding H_2 as co-reactant. What did change though were yields of propanol and propanal in product. While hydrogen was not added, reaction selectively catalyzes mainly formation of propanal meanwhile increasing amount of hydrogen fed to the reaction increased yield of propanol in expense of propanal[31].

Thermodynamics of reactions above are described as follow; 1,3-propanediol is dehydrated to allyl alcohol (thermodynamically favored K_{eq} = 3.4 x 10^2 bar at 503 K [53]) followed by dehydrogenation to thermodynamically unfavorable acrolein (K_{eg} = 0.04 bar at 503 K [53]). Allyl alcohol could also transform directly into the propanal via double bond isomeration which is rapid intra or inter molecular transfer of hydrogen which is thermodynamically favored (K_{eg} = 1.2 x 10^6 Pa at 503 K [53]).

Fast hydrogenation leads to formation of propanol and subsequent dehydration and hydrogenation leads to final product propane and propene. For the last mentioned reaction, acid catalyst is desired. For mentioned thermodynamic conditions, no propane was detected even after residence time for propanol and propanal to get to the equilibrium [54-56].

In summary support of the catalyst ZnO/Al_2O_3 was responsible for dehydration-dehydrogenation of 1,3-propandiol to acroline and metal part of the catalyst (Cu) enhance hydrogenation of acrolein to propanal and propanol [31].

Sequent effort was focused on reactions of propanal-propanol mixtures with H_2, which form C5, C6 hydrocarbons with less content of O-atoms, compare to the feedstock. Rest of the oxygen is released as water via condensation or esterification. *Figure 9* describes possible mechanism and final products that are most probably formed in this reaction.

- Dehydration of propanol to propene and subsequent hydrogenation
- aldol-type condensation happens by activation of C-H bonds at α-position to form an aldol intermediate that can further react to 2-metyl-3-pentanone and 2-methyl-pentanal or undergo decarbonylation or decarboxylation to form 3-pentanone [32]
- formation of linear C_6 alkanals and alkanones by activation of C-H bonds at β-position
- esterification reactions to form propyl propionate [57].
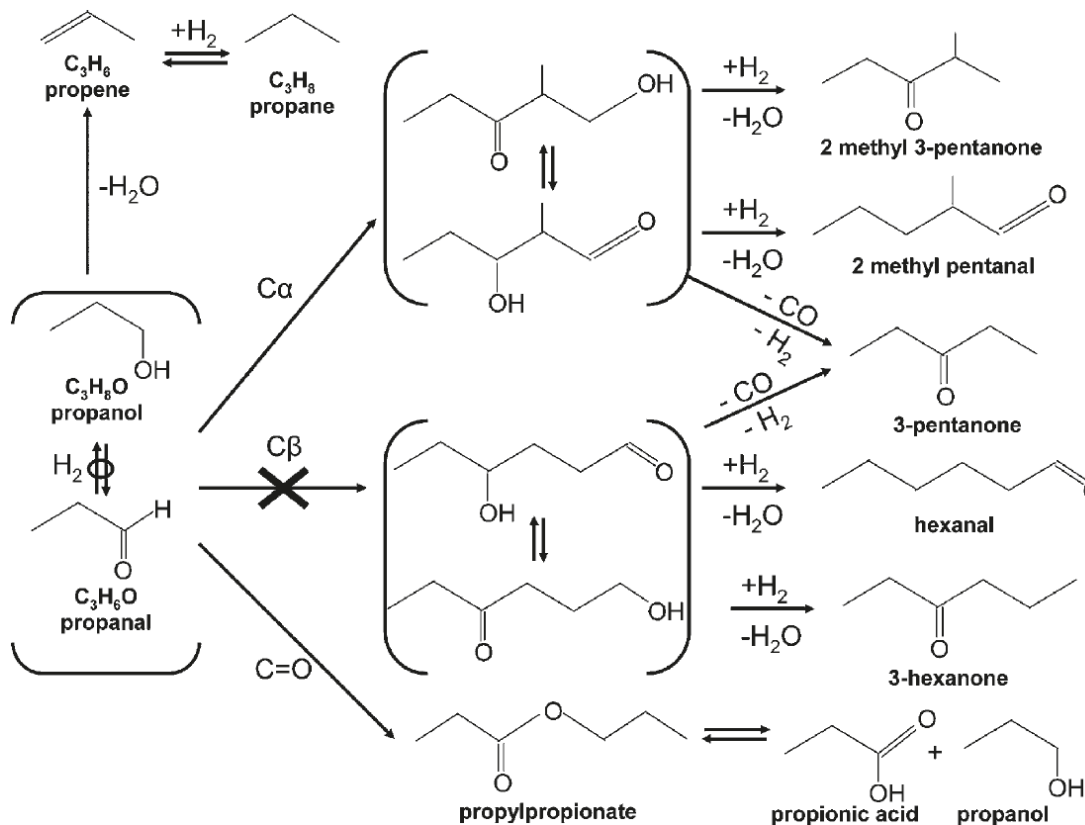
Figure 9 - Network for propanol-propanal reactions on Cu-based Catalyst[31].

From above scheme, first two products are main products if Mg/Al oxides are used. 2-methyl 3-penatanone and 2-methyl-pentanal are also products from the reaction catalyzed on Cu based catalyst the main product is however 3-penatanone as result of decarbonilation, decarboxilation.

Davda, Shabaker, Huber, Cortright, Dumesic were also searching for the catalyst to produce hydrogen from the biomass [49]. During the testing of various types of catalysts, they found some catalysts, which could be preferably used for alkanes production. Pt/Al_2O_3 with added SiO_2-Al_2O_3 is one of the catalysts where selectivity of produced hydrogen significantly decreased because all the hydrogen was consumed for the production of straight-chain compounds and minimal amount of branched isomers (cca. 5 %).

They also investigated that selectivity of produced hexane significantly increases with increasing pressure. Following *Figure 10* shows, which conditions are beneficial for hydrogen and which are preferable for alkanes production.
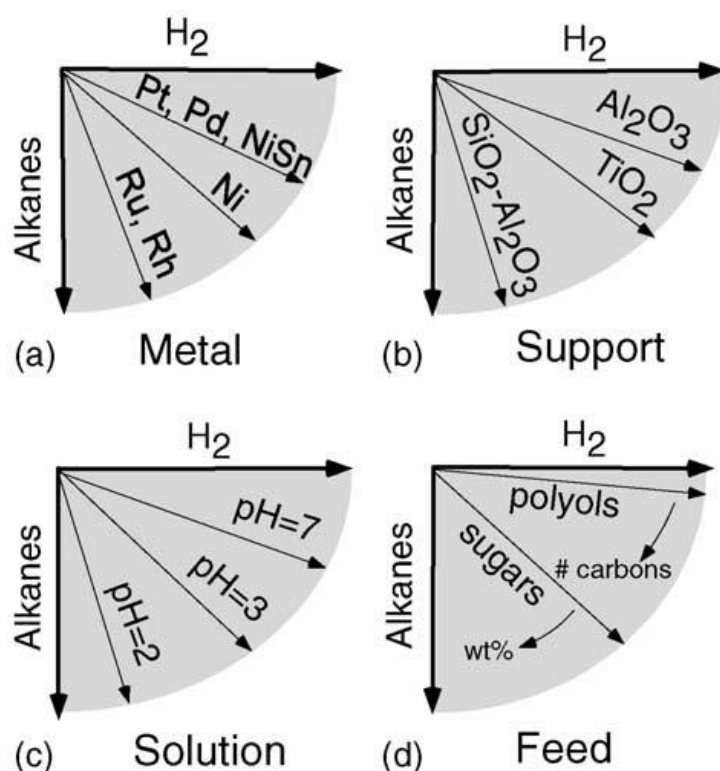
Figure 10 - Factors controlling the selectivity of the aqueous-phase reforming process.

Davda et. al. claim, Ni but should be the best option for production of alkanes however due to sintering it loses its dispersion by the time and tend to deactivate. Use of Ru and Rh catalyst is probably best choice for alkane production over hydrogen production. Following conclusions they found for the support are as follow: highly acid feed is beneficial for alkanes production against neutral feed which favorable for hydrogen production.

Hydrogen, like it has been mentioned above, is key source in production biofuels from biomass. As feedstock for bio-hydrogen production various types of oxygenates could be used. Namely it is glucose, sorbitol, glycerol, ethylene glycol and methanol. There are two main ways how to utilize hydrogen. First is to use it directly as energy to the hydrogen fuel cells. Second option is to use hydrogen as co-feed in production of liquid biofuels [28].

Various types of catalysts have been used in hydrogen production research. Rh, Ru, and Ni based catalysts were among of studied catalyst and apparently they happened to favor alkanes over hydrogen production [58]. Mentioned metals prefer cleavage of C-O bonds over C-C bonds. Same types of studies have been done for

catalysts support. Interesting results were obtained for SiO_2 and Al_2O_3 which have lower selectivity for the hydrogen production and rather favor formation of light alkanes *2–III*.

Some lighter alkanes could be produced without an external source of hydrogen as production of C_6 hydrocarbons from sorbitol. Cleavage of C-C bond is followed by production of hydrogen which is afterwards consumed in deoxygenation reaction *2–IV* [28].

2–III

$$C_6H_{14}O_6 + 6H_2 \rightarrow C_6H_{14} + 6H_2O$$

2–IV

$$C_6H_{14}O_6 \rightarrow \frac{13}{19}C_6H_{14} + \frac{36}{19}CO_2 + \frac{42}{19}H_2O$$
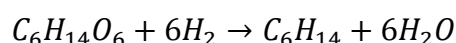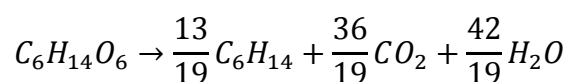
Nevertheless, selectivity to desired product can be improved introducing hydrogen as an external feedstock. On the other hand, disadvantage of this process lays in limitation of the length of formed hydrocarbon chain. Up to six carbons chain can be formed which unfortunately makes product too violate to be used in high concentration as liquid fuel [28].

Operating condition for this process had to be carefully set up. Suggested optimal conditions are low temperature, elevated system pressure, and high oxygenate feed concentration for the C-O bond cleavage.

H_2O and CO_2 act as inhibitors for ketonization and aldol-condensation catalysts [59, 60], [61]. CO_2 is produced from kentonization reaction and presence of 5 % CO_2 in the feed leads to approximately 90 % reduction of catalytic activity and even a small concentration of water in the feed can significantly reduce catalytic activity. Especially if cerium/zirconium based catalysts are used the inhibition can significantly influenced yield of the product. Very stable against deactivation by CO_2 and H_2O is Pd/ZrO_2 based catalyst. This choice seems to be advantageous because then ketonization and aldol-condensation would take place in single reactor with two catalysts beds. First bed stacked with $CeZrO_x$ followed by Pd/ZrO_2. This process enables collide two processes into one single with no need of separation intermediates.

Moreover results from two stage process and single reactor are similar [28]. $Pd/Ce_1Zr_1O_x$ was used as catalyst with H_2 co-feed for the reaction [62].

Reaction of short chain oxygenates to C_{12+} hydrocarbons could be performed over $Pd/Ce_2Zr_5O_x$ and Pd/ZrO_2 which show better resistivity against water or CO_2 poisoning compare to just ceria based catalysts for instance. Moreover, it is highly active towards aldol condensation of 2-hexanone. Primary C_{12} products were formed however due to higher acidity of Pd/ZrO_2 catalyst C_{18} ketones and aromatic products were formed as well [62].

2.5   Different approaches

Above mentioned literature and knowledge gained from the papers served mainly as guide for experimental part of this project. However among the literature concerning the production of biofuels there were several inspirational approaches, which one of them deserves to be mentioned in this work too.

2.5.1   Solid nanoparticles for biofuel upgrade

Crossley, Faria, Shen, and Reasco presented second and last interesting approach mentioned in this part. This research was aimed on carbon nanotube catalyst doped with silica and palladium [67, 68]. Carbon nanotubes and silica create and stabilize interface between two liquids which are at normal conditions immiscible and palladium and silica catalyze the reaction as aldol condensation and hydrogenation of compounds dissolved in the aqueous phase turn them to hydrophobic compounds which afterwards pass into the oil phase where remain. Appearance of the system is shown on the *Figure 11*.
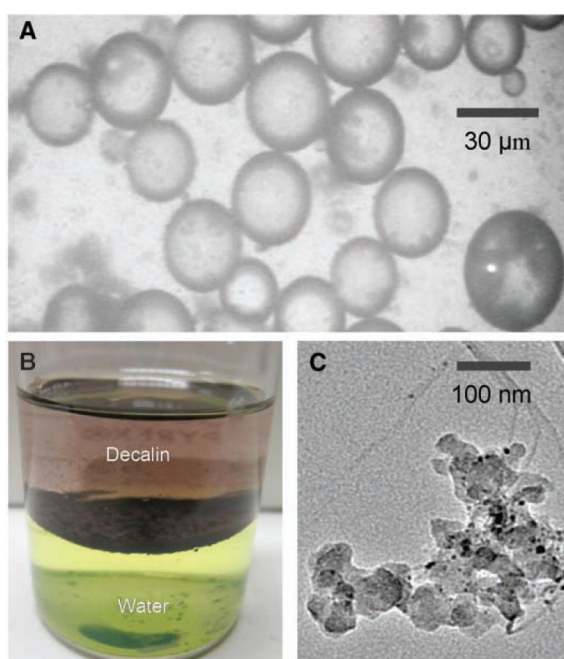
Figure 11 - (A) Optical microscopy image of a water-in-oil emulsion formed by sonicating a 1:1 mixture of decalin and water in the presence of 5 %wt Pd/SWNT SiO2 nanohybrids. (B) same system before sonification. (C) TEM image of the 5 % wt Pd/SWNT-SoO2 nanohybrid[67].

Therefore, if product is unstable in one phase under specific reaction condition it could pass into second phase. Formation and also extraction of the phases is safer and easier in terms of the product i.e., need for distillation is unnecessary which is beneficial if oil phase contains violate compounds.

Fact that most of the reactants are in the aqueous phase makes this catalyst so attractive. If the common catalyst is used for the reaction in aqueous phase, it would probably sink to the bottom of the heavier phase (water) and only compounds soluble in the water would be then converted. Therefore majority of researchers works with the gas phase.

The hydrophilic hydrophobic balance and assemble water-in-oil or oil-in-water emulsion could be tuned by modifying the composition of carbon nanotubes and silica [69]. Two of the challenges are to add transition metal on the catalyst which provides hydrogenation reaction and add there solid base oxide which will catalyze condensation reactions. Scientists used two ways how to prepare catalyst. First was deposition of Pd onto the single-walled carbon nanotube (SWNT) – silica nanohybrids, via wetness impregnation, which leads to preferential deposition of Pd onto the silica side. Second way was to replace SiO_2 with MgO as support this led to higher defection of CTN compare to first one. On the other hand, they are more effective in retaining Pd particles. Replacing silica with the magnesium oxide improves the properties of the catalyst by higher efficiency in stabilizing of emulsion, and it improves catalytic activity for base-catalyzed reactions such as aldol condensation [67].

Experiments of this catalyst were run in several temperatures and it was found out at 100 °C only hydrogenation appeared, at 200 °C hydrogenolysis became dominant, and at 250 °C the main reaction was decarbonylation.

3 Experimental part

In the literature part was mentioned that direct catalytic conversion of wooden biomass to liquid fuels happens in two main steps. First part is to transform cellulose, hemicelluloses and lignin into to basic chemical compounds which it is assembled of (mainly basic sugars, cyclic C_6 and C_5 oxygenated hydrocarbons). These compounds are then further transformed to polyethylene glycol and polypropylene glycol.

Second step is focused on conversion of C_2 and C_3 polyalcohols to C_{6+} hydrocarbons with concurrent reducing of oxygen content so the final product is suitable for combustion in car engines. Main idea is therefore to test several catalysts and examine which support and metal would be best choice for second step in direct biomass conversion to liquid fuels. By the best choice is meant catalyst with the highest conversion towards C_{6+} hydrocarbons. Moreover, all materials used for this project were carefully chosen in respect to theirs relatively low price. In addition, reaction conditions are set to be economically beneficial for large-scale production. Idea is to find cheap catalyst, which would be effective in undemanding reaction conditions i.e., pressure close to atmospheric pressure and reaction temperature close to ambient temperature. Looking for such conditions is the only way to gain access to future competitiveness of fuel produced from biomass and crude oil.

This work follows up the research of Professor De Chen and doctor Jun Zhu who are intensively interested in this topic for a long time. According to findings they made, possible reaction pathways are as it is suggested in *Figure 12*.

To every reaction, beside 2 grams (3 grams of catalyst were used for deactivation tests) of tested catalyst, 0,5 gram (0,75 g) of Cu/SiO_2 was added to obtain mixture of alcohols and aldehydes. This is fundamental step for aldol condensation to occur.

It was assumed that addition of metal to the TiO_2 improves yield of desired products, which are C_{6+} hydrocarbons and suppress formation of undesired byproducts (esters and ethers).
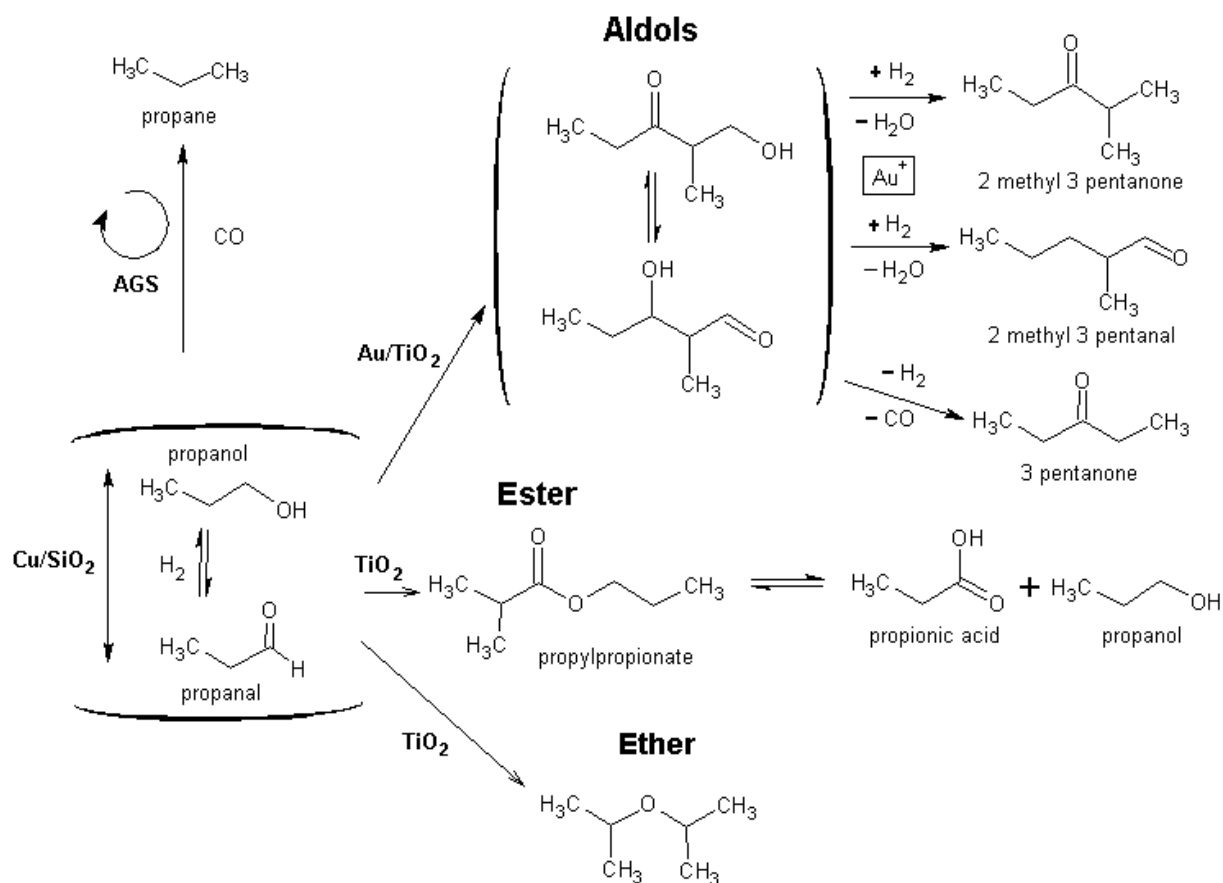
Figure 12 - Suggested reactions pathways.

3.1 Synthesis of catalysts

Some of the catalysts tested in this project were already prepared by doctor Zhu. Some of them were prepared after consultation with supervisors.

3.1.1 Metal oxide calcination

Best results in this field so far were obtained with titanium oxide, hence next step was to find out how the yield of the product would be influenced by calcination temperature of TiO_2. Therefore four TiO_2 catalysts were calcinated ranging from 300 - 600 °C. Titanium oxide (ACROS ORGANICS) was calcinated in the high temperature calcination furnace (NABERTHERM) for three hours under static conditions. Besides titanium, several other catalyst's supports were prepared and calcinated at certain temperatures. These metal oxides were carefully chosen to range from "acid" to "basic"

to see how this property will influence reaction. Special attention was paid to pick catalysts with possibly high surface area, which allow us to focus on other parameters of the catalysts rather than surface area. As basic catalysts CaO and MgO were selected, they were labeled as superbases or strong basic catalysts. From the other side of this spectrum SiO_2 and CeO_2 were selected to represents acid catalysts, and of course TiO_2 that would belong in the middle of this spectrum.

3.1.2   Wet insipient method

Various types of catalyst were prepared by wet insipient method, namely 5% Au/TiO_2, 5% Cu/SiO_2, 5% Ag/MgO, and several 5% Ag/TiO_2 Amount of deposited metal was calculated 3–I, 3–II, 3–III:

3–I

$$m_{Met} = m_{cat} \cdot w_{Met}$$

3–II

$$n_{Met} = \frac{m_{Met}}{M_{Met}}$$

Correction for precursor purity

3–III

$$n_{Met} = n_{MetPrec} \cdot x$$

$$m_{MetPrec} = n_{Met} \cdot Mw_{MetPrec}$$

where:

mMet	metal mass
mCat	total weight of the catalyst
wMet	mass friction
nMet	molar amount of constituent
nMetPrec	molar amount of precursor

mMetPrec   mass of the precursor

MwMetPrec   molar weight of the precursor

x   purity of the precursor

As metal precursors $HAuCl_4 \cdot H_2O$ (99,999 % Sigma - Aldrich) for Au, $Cu(NO_3) \cdot 2{,}5\ H_2O$ (Fluka) for Cu and $AgNO_3$ (99,8 % MERCK) for Ag were used. As support TiO_2 (ACROS ORGANICS) and MgO (Merck) were used.

Calculated amount of metal precursor was dissolved in the distilled water and dropwise added onto catalysts support under continuous stirring, until support was saturated. Properly stirred mixture was left in the fume hood overnight to dry out and then calcinated in high temperature calcination furnace (NABERTHERM) at set temperature. All catalysts were crushed to the powder to improve homogeneity after calcination.

3.1.3   Preparation of strong basic catalysts

Magnesium oxide was prepared according to J. I. Di Cosimo et al. [70] who prepared high surface strong basic magnesium oxide for theirs project. Instructions were following; to 10 grams of commercially purchased MgO (MERCK) was slowly added distilled water during which catalyst was continuously stirred. Whole solution was heated up to 80 °C for 4 hours. Leftover distilled water was removed during drying in the oven at 85 °C overnight. This process should transform MgO to hydroxide $Mg(OH)_2$. To get back to MgO, dried catalyst had to be calcinated. Calcination was set to 2 h at 350 °C and then 8 h at 500 °C. This calcination program should secure that entire $Mg(OH)_2$ will be transformed back to MgO.

Preparation of CaO was inspired by article written by H. Zhu [71] who claims that dipping of CaO in the solution of ammonium carbonate will change CaO from strong basic catalyst to superbase. Process of preparation was following; 12 g of CaO (MERCK) was dipped into 0,12 g/ml ammonium carbonate (ALDRICH) solution. Whole mixture was kept under continuous stirring for 30 minutes and then filtered. Wet catalyst was put to the oven to dry out at 110 °C overnight. Finally dried CaO was milled and calcined at 500 °C for 1,5 h.

3.1.4   Preparation of TiO₂ coated on the CNTs

Titanium dioxide or titanium based catalysts proved to be most effective after series of experiments in this project. However, the effort is to improve properties of the catalysts even further. One way how to reach this goal is to improve catalysts surface area via coating TiO_2 onto carbon nano-fibers (CNF).

Five grams of prefabricated CNF were mixed with 150 ml of nitric acid and boiled at 100 °C for one hour. After that, mixture was removed from silicon bath and left to cool down to room temperature. Solution was filtered and entire step was repeated three times to make sure that all traces of metal and impurities from prefabricated CNF will be removed. Washed CNF were kept in the oven at 100 °C overnight to dry out.

Dried CNF were mashed into the fine powder and mixed with the coating solution, which in this case was $C_{12}H_{28}TiO_4$ (Fluka). Amount of solution was calculated to make 20 % [wt] loading of TiO_2 on fibers. Coating solution was dissolved in ethanol and entire volume of coating solution and ethanol was approximately three times volume of treated CNF so that all CNF were fully immersed. Fibers and liquid solution were sonicated for 15 minutes. Fibers were filtered and kept in the oven overnight at 100 °C. Finally fibers were calcinated in the high temperature furnace at 350 °C for 4 hours.

3.2   Catalyst characterization

Temperature programmed desorption (TPD) analysis with reduction of catalyst was used to examine abundance of basic sites of the catalyst. Sample was weighted and inserted into the NETZS STA 449C JUPITER TPD analyzer. Catalyst was heated up to 350 °C at rate of 10 K/min and kept at 150 °C for one hour under gas flow of argon 50 ml/min. Afterwards it was cooled down to 30 °C under cooling ramp of 20 K/min under 50 ml/min argon. Gas flow of argon was partly switched to CO_2 both to 25 ml/min and kept at 30 °C for 1 hour. Hour later gas flow of CO_2 was turned off and just 25 ml/min of argon was used for 30 min. Finally sample was heated up to 900 °C at 10 K/min rate, Ar 25 ml/min then analysis was stopped and sample was cooled down to room temperature. Gas outflow from the TPD was again analyzed with NETZS AËRLOSQMS 403C MS detector.

Total surface area (BET) of the catalyst was measured with Tri Star 3000 Surface Area and Porosity Analyzer. Calculation of pore volume, pore size, and pore surface was calculated by Barrett-Joyner-Halenda (BJH) method.

Method used to analyze catalysts properties was XRD. Powder X-ray diffractograms were recorded on a Bruker D8 Focus diffractometr using Cu Kα radiation. Diffractograms were identified using the ICDD PDF 4+ 2011 database.

Last characterization was done with TEM JEOL2010 microscope operating at 200 kV. This device is able make images of our catalyst in nanoscale so this method was used to see how the coating of TiO_2 on CNF is.

3.3   Activity test

Reaction activity test was carried out using fixed bed reactor system with integrated gas flow, mass flow controller, and pressure modules. Temperature was controlled with separate temperature controller. Thermocouple was located right above the catalyst bed. Two grams (3 grams respectively) of tested catalyst together with 0,5 gram (0,75 grams respectively) of 5 % $CuSiO_2$ were positioned on quartz wool inside 15 mm ID reactor. Prior to reaction catalyst was reduced *in situ* for two hours in mixture of 30 % [mol] H_2 and 70 % [mol] N_2 at 230 °C, 300 °C respectively. Reactant gas mixture consists of 7,42 ml/min of propanol, 7,42 ml/min of hydrogen, 22,27 ml/min of nitrogen (100 ml), and 22,27 ml/min of nitrogen (250 ml). All reactants were in gas phase. Fed of liquid propanol was evaporated in evaporator at 180 °C before it entered reactor. Gas mixture after the reaction was condensed in the condenser. Different conditions were used for deactivation test, more about that in **4.5.1 Deactivation test**. Liquid product was collected after 4 hours and 20 hours and analyzed with 5890 Series II Gas Chromatograph. Catalyst was tested under two different reaction conditions: 230 °C, 1,2 bars and 300 °C, 1,2 bars. Layout of the reactor system is shown on *Figure 13.*
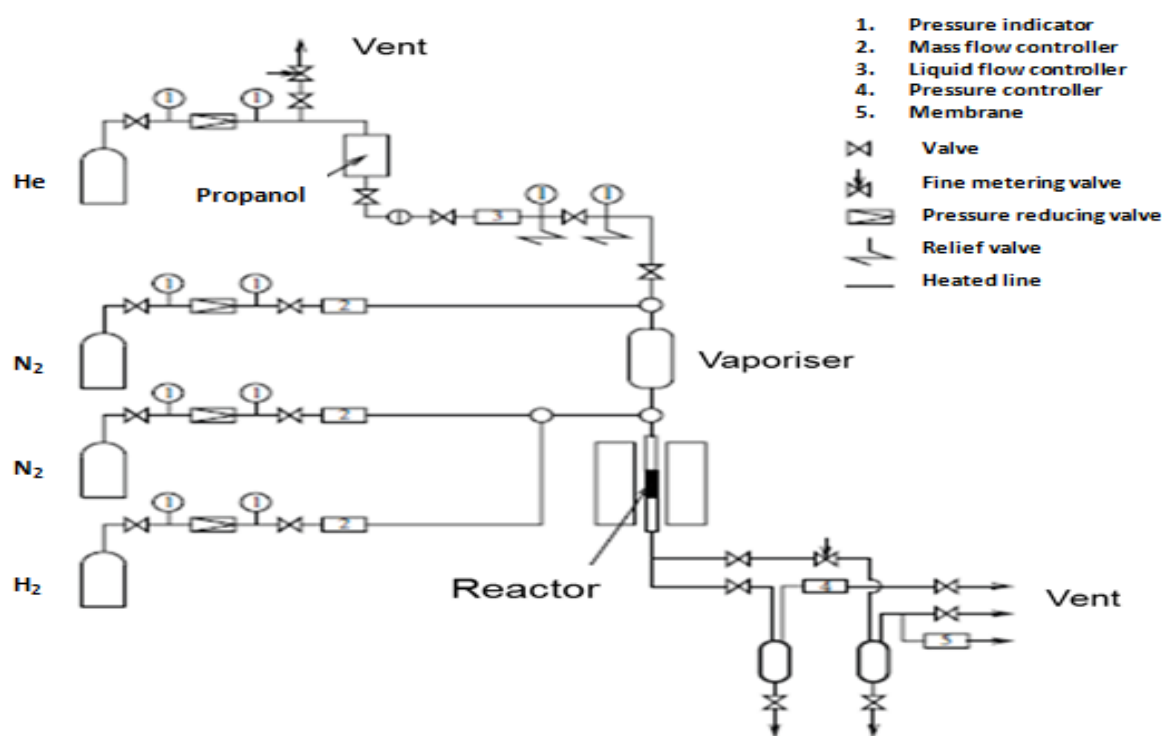
Figure 13- Reactor system layout.

4 Results and discussion

4.1   TPD analysis

Earlier in this text, it was suggested that activity of the catalyst for aldol condensation is closely linked with amount of acidic and basic sites of the catalyst. Therefore, TPD analysis with CO_2 as probe molecule was used to detect amount of basic sites of catalyst. Findings could be then link with results from activity test to see if there is any possible correlation between them. Signal from MS as function was plotted against temperature. Signal was normalized by dividing the signal value with amount of catalyst used for TPD analysis. Results are shown on following Figure 14.
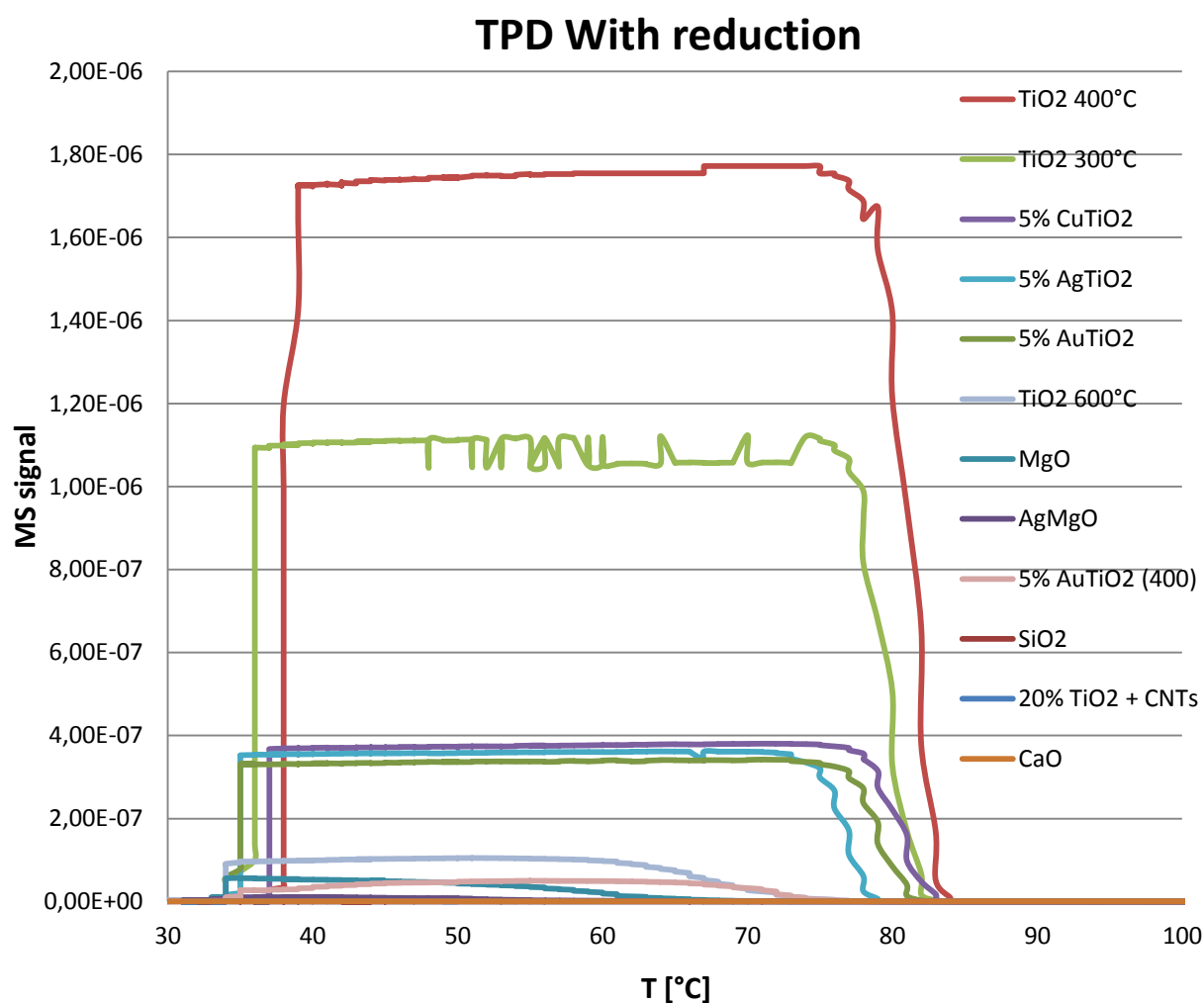
Figure 14 - results from TPD with reduction analysis

Titanium oxides doped with metals have significantly lower basic character compared to titanium oxide alone. In addition, calcination temperature of TiO_2 obviously affects abundance of basic sites. Increasing temperature of calcination distinctly increase amount of basic sites of the catalyst.

During this project some problems with TGA analyzer appeared. No signal from MS detector was measured after analysis. TGA needed to be repaired and some parts were replaced. TGA was out of order for significant period and in the very end of the semester it was repaired again and fully functional. Majority of the tested catalysts were analyzed. Unfortunately few results which were taken before device repair; namely TiO_2 400 °C, TiO_2 300 °C, 5 % $CuTiO_2$, $AuTiO_2$ and $CuTiO_2$, which all of them expose the highest abundance of basic sites in Figure 14 were measured on MS analyzer before TGA collapsed. There was no time to re-take tests for these catalysts again so obtained results is necessary evaluate carefully. We can only guess until which level results were influenced by maintenance. However, from Figure 14 it is obvious that results were influenced strongly. On the other hand from results taken after maintenance it is clear that most basic catalyst has TiO_2 600 °C and all titania based catalyst showed very good results in experimental part.

Of course to have even more accurate information, about our catalysts, it would be highly desirable to run also TGA with ammonia instead of CO_2, to find out abundance of acidic sites, and then make even more precise conclusion. Unfortunately, unexpected events prevented us from doing further experiments.

4.2   BET analysis

Results from BET are shown in Table 2. Addition of metal to the titanium oxide will not influence its total surface area nor pore surface. On the other hand pore size was drastically increased after metal deposition and slight increase is also apparent in pore volume. Important criteria in selection of catalysts for this project was theirs surface area which should be as high as possible. Only exception was CaO, which was "superbase", and so it was important to try how this property will influence the reaction, and CeO_2 which contrary is strong acid catalyst. Several batches of $AgTiO_2$ catalyst were prepared, not all of them were although tested. For instance one labeled as 5 % $AgTiO_2$ (2) was not even tried out due to its low surface area.

From results obtained from BET analysis it is obvious that coating of TiO_2 onto the fibers greatly improve surface of the catalyst. Compare to titanium dioxide itself, coated TiO_2 on fibers have approximately twice as big surface area, same for pore surface area and three times bigger pore volume.

Table 2 - Data obtained from BET analyzer

Catalyst	BET Surface Area [m²/g]	Pores Surface [m²/g]	Pore Volume [cm³/g]	Pore Size [Å]
TiO₂ 300 °C	48,8	51,7	0,105	86
TiO₂ 400 °C	54,5	57,4	0,115	85
TiO₂ 600 °C	41,2	43,3	0,080	77
5% AuTiO₂	46,0	52,3	0,302	262
5% AgTiO₂	44,5	47,1	0,192	173
CaO	6,9	7,4	0,011	61
MgO	120,4	138,9	0,477	158
CeO₂	4,1	4,5	0,008	79
SiO₂	302,4	364,7	0,631	83
5% Ag/MgO	68,2	75,1	0,601	206
5% AgTiO₂ (2)	28,2	29,2	0,213	118
20 % TiO₂ + CNTs	109,2	107,5	0,315	78
5% AgTiO₂ (3)	44,0	48,0	0,367	180

4.3 TEM imaging

The catalyst was characterized by TEM on a JEOL2010 microscope operating at 200 kV. The sample for TEM study was prepared by dispersing in ethanol and depositing onto a carbon-coated grid. Doctor Zhu took following images of 20% [wt] TiO2+CNT, which are shown on Figure 15.
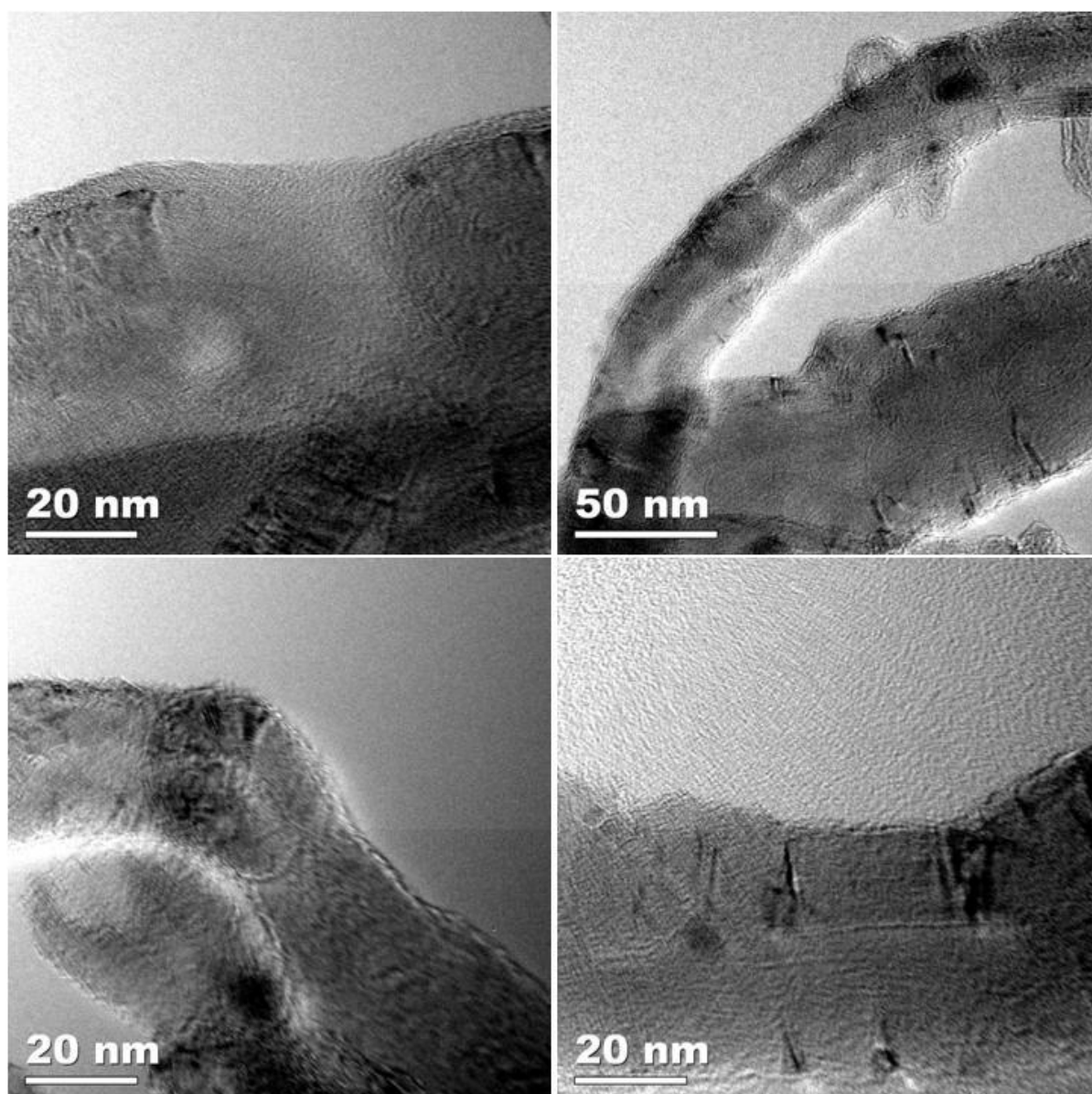
Figure 15 - TEM images of 20% [wt] TiO$_2$+CNT

Closer look reveals that there is an obvious thin layer of TiO_2, which is coated nicely on carbon nanotubes. It is easier to see it on Figure 16. Coating of TiO_2 onto carbon nanotubes besides it is very easy has one great benefit. How it was shown earlier in BET analysis, it more than doubles surface area of TiO_2, which is greatly beneficial for our purposes.
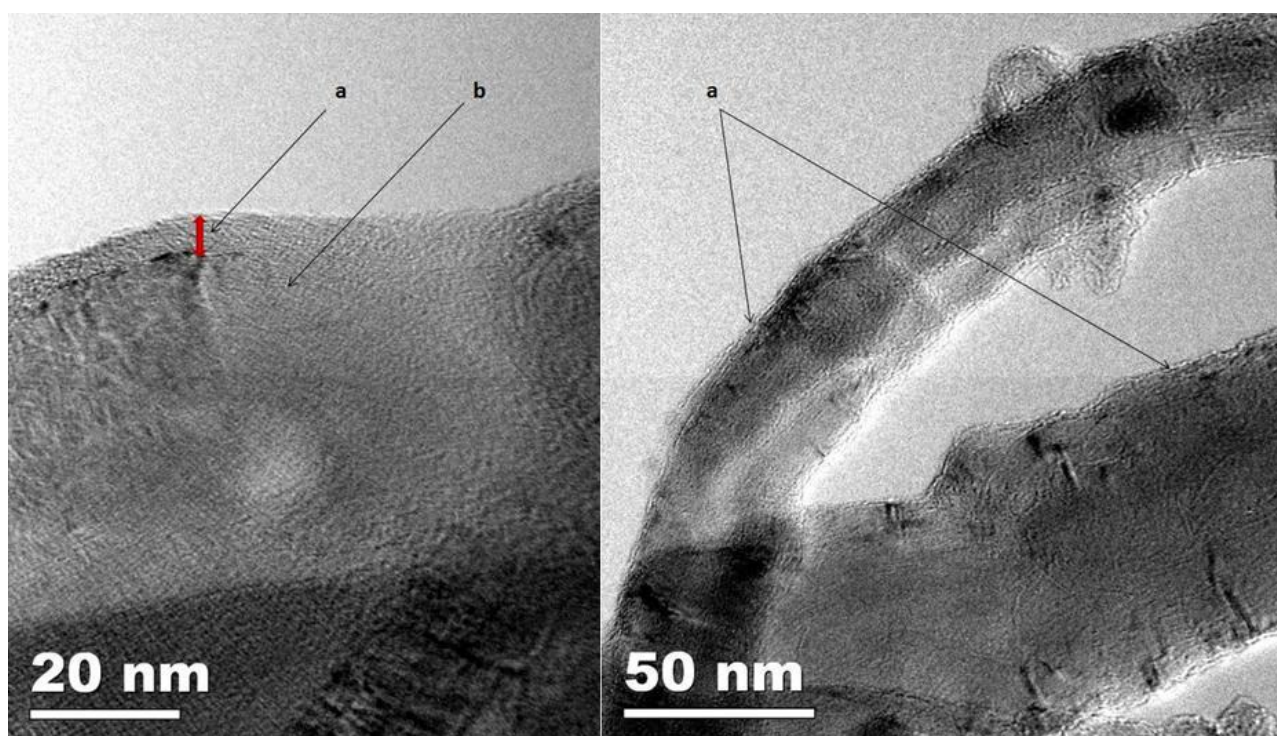
Figure 16 - TEM images of 20 % [wt] TiO_2+CNT catalyst; a) TiO_2 coating on b) carbon nanotube

4.4   XRD analysis

Powder XRD patterns of the TiO_2, Au/TiO_2, Ag/TiO_2 are presented in *Figure 17* bulk composition of each sample was confirmed by comparing XRD patterns with standards form ICDD PDF 4+ 2011 database for anatase (86-1157), rutile (21-1276), Au (01-2616), and Ag (04-0783).

Peaks for titania, exhibiting peak at ∼ 25,3 °, 37,8 °, and 48,1 °, that are consistent with the (1 0 1), (0 0 4) and (2 0 0) planes associated with tetragonal anatase. For rutile tetragonal structure corresponding peaks are in ∼ 27,4 °, 31 °and 54,5 ° that are consist with the (1 1 0), (1 0 1) and (2 1 1) planes.

Relatively high loading of metals led to detection of crystalline planes especially of peaks representing gold in ∼ 38,1 ° and 44, 3° that are (1 1 1) and (2 0 0) planes. For silver/titania catalyst there were several overlapping with titania anatase.
After detail exploration of peaks for titania oxide calcinated at 300 °C, 400 °C and 600 °C, besides slight shift of TiO_2 300 °C peaks, is noticeable increasing crystallinity of TiO_2 catalyst and increasing amount of rutile planes.

Also in silver titania catalyst there are two peaks marked with star which did not correspond to any possible compound in database. Less possible option is that it is some chemical composite from chemicals used in catalyst preparation. Most likely, it is some kind of impurity, which contaminated this catalyst during the process.

Third batch of silver titania catalyst was prepared and after results from BET confirmed that surface area is similar, XRD was done for this sample to see whether it is also similar in composition. Result is shown in Figure 18 and it is obvious that peaks from second batch are less sharp, which could be due to lower calcination temperature used for this catalyst. First one was calcinated at 500 °C and second one only at 400 °C it is highly possible that this resulted to a different properties of second catalyst, although it has no influence on catalyst's surface area.

Another XRD spectrum was taken for magnesia catalyst to see how deposition of silver influences properties of the catalyst's support. From BET results we know that silver deposition on magnesium oxide drastically reduces surface area of the catalyst and increase pore volume in the same time. In case of XRD, besides appearance of peaks for silver, there are no changes in the catalyst, results are in Figure 19.

Last spectrum belongs to 20% [wt] TiO_2+CNT catalyst. This test was carried out to see whether titania will appear on the XRD spectra and if yes what phases will be there. Only carbon phase was recognized by the D8 Focus, and we believe this is due to fine coating of titania on the carbon fibers. Titania layer is simply too thin to be detected by the scanner.

XRD is important analysis, however for our purposes it is not as important as results from BET or TGA, so only most interesting catalysts were selected to be tested on XRD.
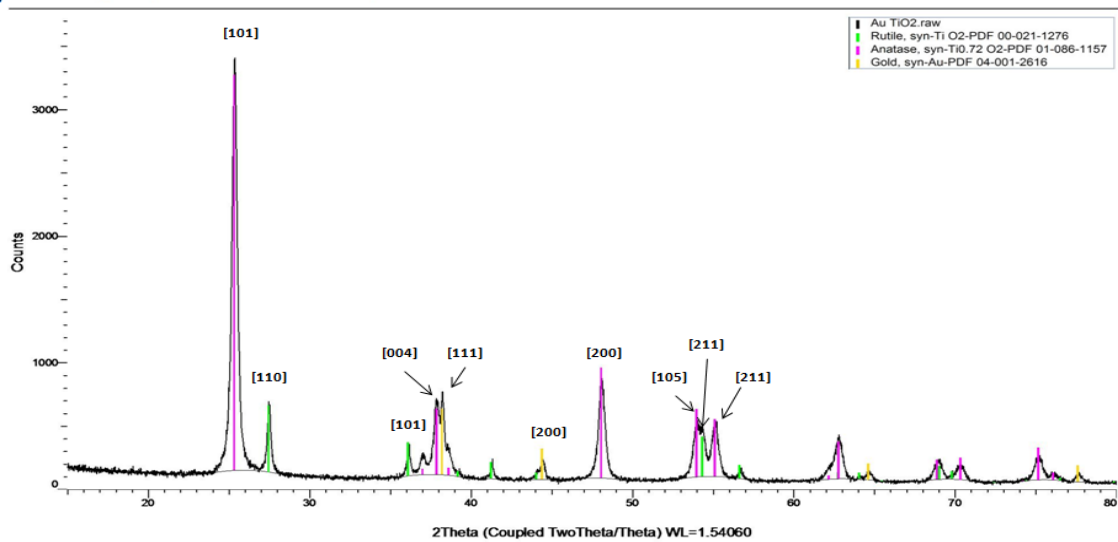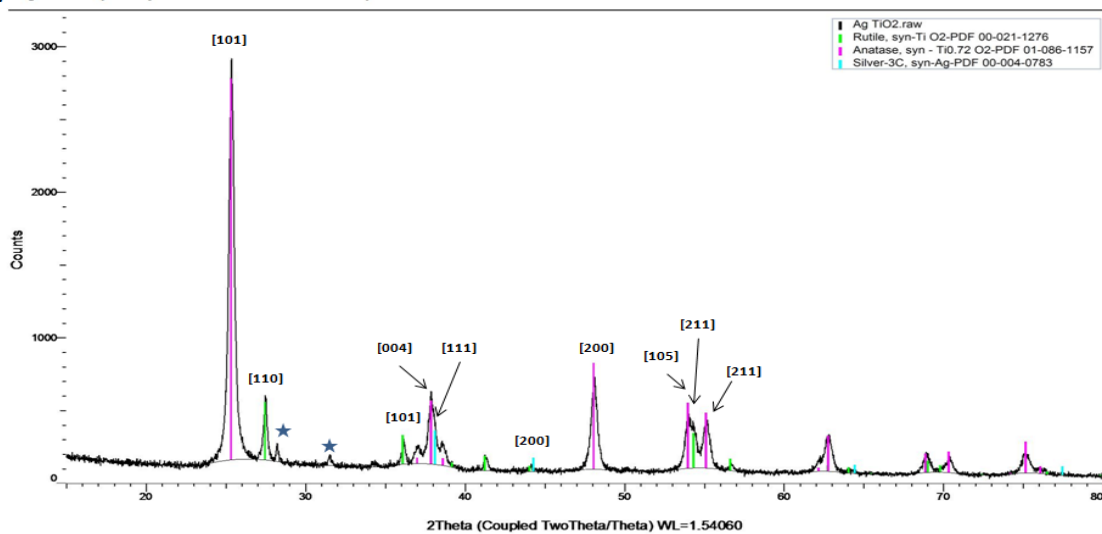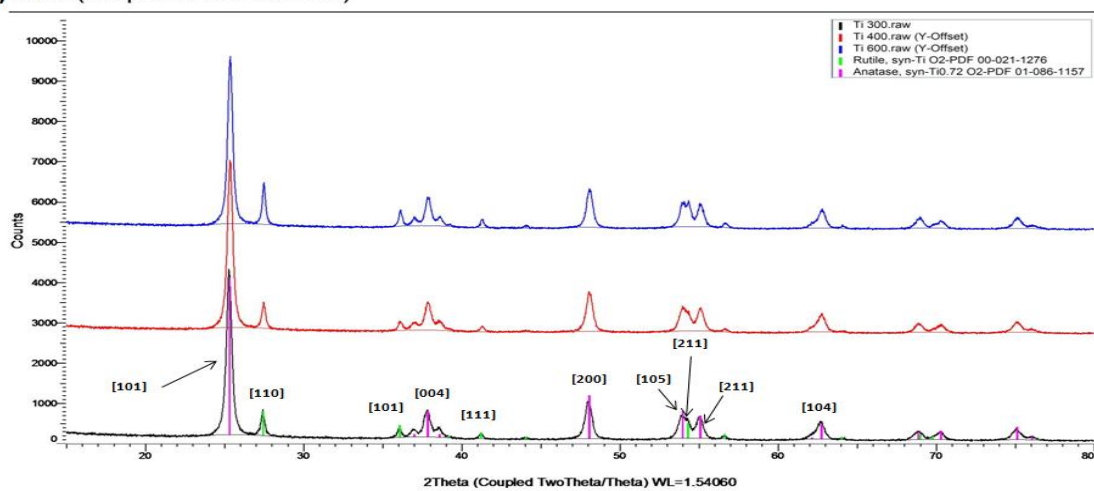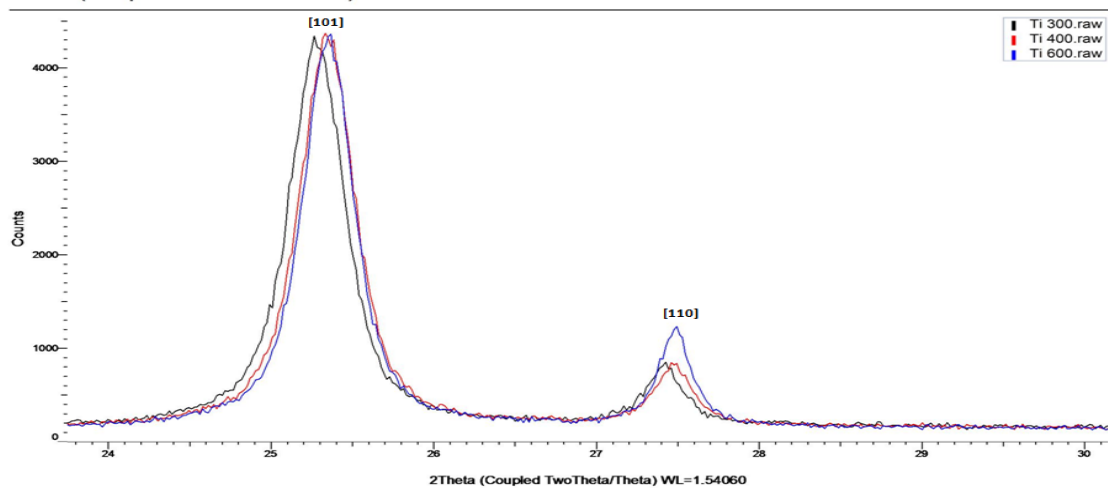
Figure 17 - XRD patterns for a) Au/TiO$_2$, b) Ag/TiO$_2$, e,f) TiO$_2$ calcinated at 300 °C, 400 °C and 600 °C.
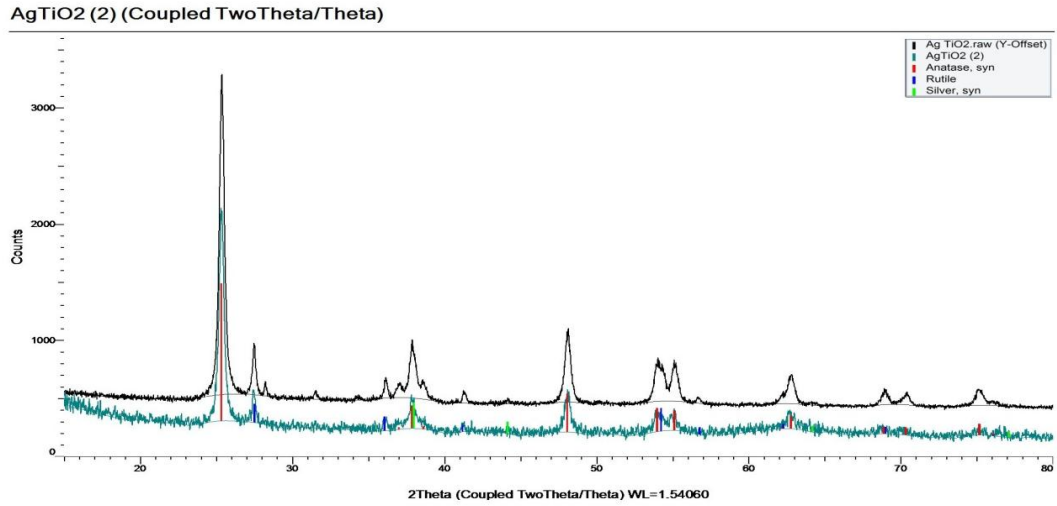
Figure 18 – comparison between to different batches of AgTiO$_2$ catalysts
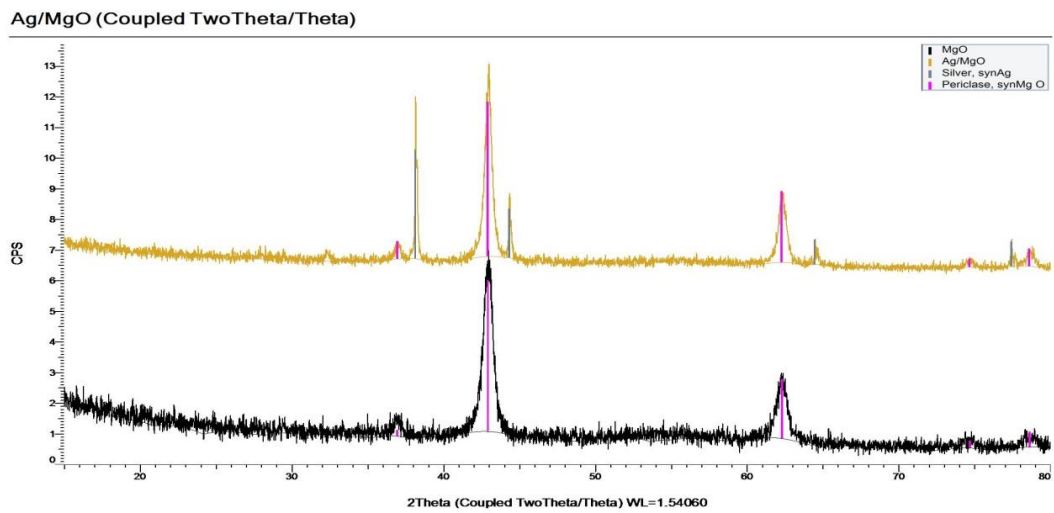
Figure 19 - comparison between pure MgO oxide and 5 % Ag/MgO
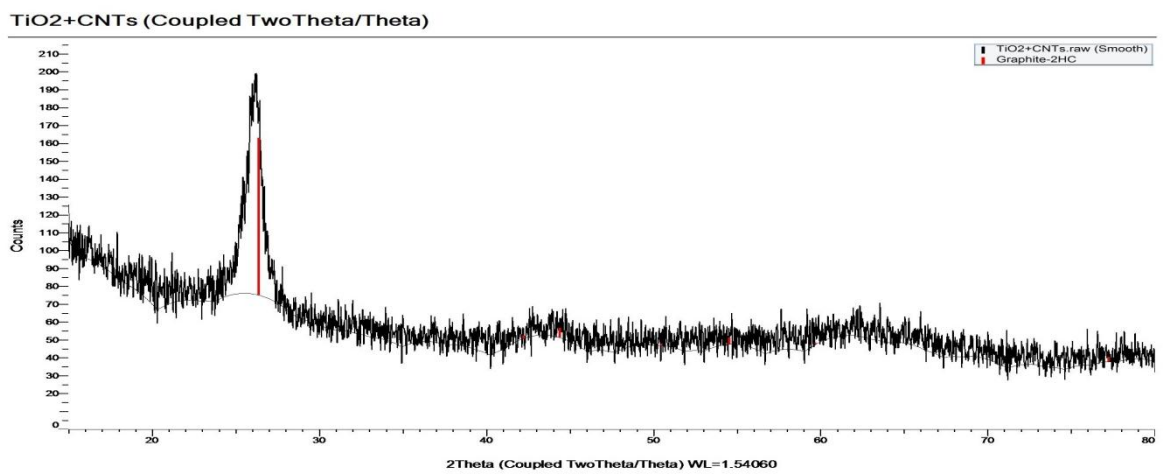
Figure 20 - XRD spectrum of 20 % [wt] TiO$_2$+CNTs

4.5   Activity test and deactivation of the catalyst

Product was analyzed with GC and obtained spectra were distinguished to see what product was formed in the mixture. From the area of each peak, amount of chemical compound presented in the collected product was calculated together with conversion and selectivity.

Obtained product after reaction on titania based catalysts was two-phase system. Lighter, oil phase full of higher hydrocarbons and transparent phase, containing mainly propanol feed. We believe this is an important observation. This is a reason, why all graphs are divided to titania based and the rest. For each catalysts ratio between oil and transparent phase was different but more or less we can say it was around 25 % [wt] of transparent phase and 75 % [wt] of oil phase.

Following equations were used to calculate the selectivity 4–I, 4–II, 4–III and 4–V. Conversion was calculated from carbon mass balance. Response factor for most C6 hydrocarbons presented in liquid mixture was founded by Yingpeng Zhen. Unfortunately, finding response factor for C9 and higher hydrocarbons is very difficult and time-consuming process and therefore universal value was used in calculations. Nevertheless only small deviation is made by using this value.

4–I

$$\text{weight rate} = \frac{\text{peak area}}{\text{response factor}}$$

4–II

$$\text{weight \%} = \frac{\text{weight rate}}{\Sigma \text{ weight rates}}$$

4–III

$$\text{mol rate} = \frac{\text{weight \%}}{\text{Molecular weight}}$$

$$\text{mol \%} = \frac{\text{mol rate}}{\Sigma \text{ mol rates}}$$

4–IV

$$\text{number of } C_6 \ (C_9, C_{12}) = \text{mol \%} \cdot \text{number of carbons in hydrocarbons structure}$$

4–V

$$\text{selectivity} = \frac{\Sigma \text{ number of } C_6 \ (C_9, C_{12})(\text{rate})}{\Sigma \text{ number of } C_{6+} \ (\text{rate})}$$

Conversions and selectivity were plotted in the following graphs Figure 21-31. Product after reaction on titania based catalyst was two phase system. One the top there was lighter oil phase and below on the bottom there was aqueous phase. Only results from oil analysis of oil phase are presented in this project, although results for both phases were similar. Results from aqueous phase are not presented because water fraction is not known. External standard need to be obtained in order to find concentration of water in the sample. It is planned for further research, unfortunately it is not involved in this work. In reality, aqueous phase to oil phase varied around 25 % [wt] ± 5 % of aqueous phase. From tests, which we ran, it could be safely said that amount of transparent phase was closer to 20 % [wt] so there were more desired oil phase.

Figure 21 – 30 - conversions and selectivity of tested catalysts
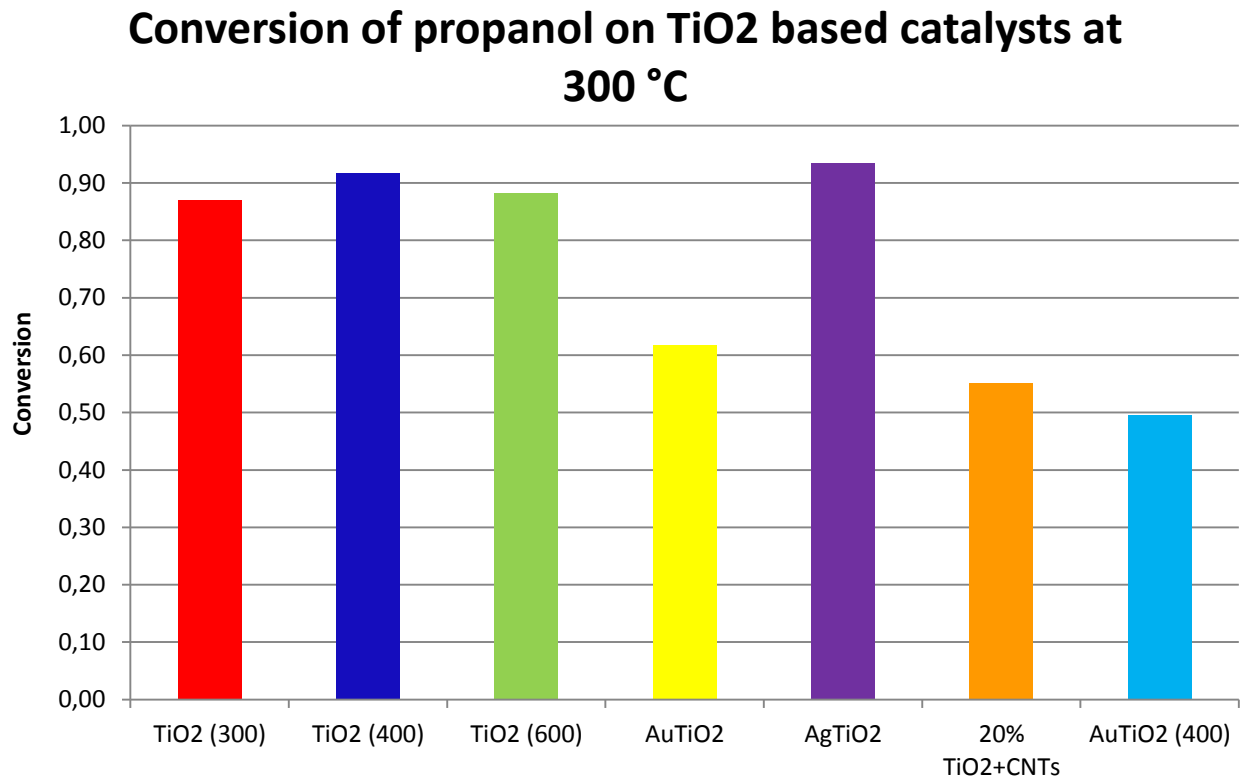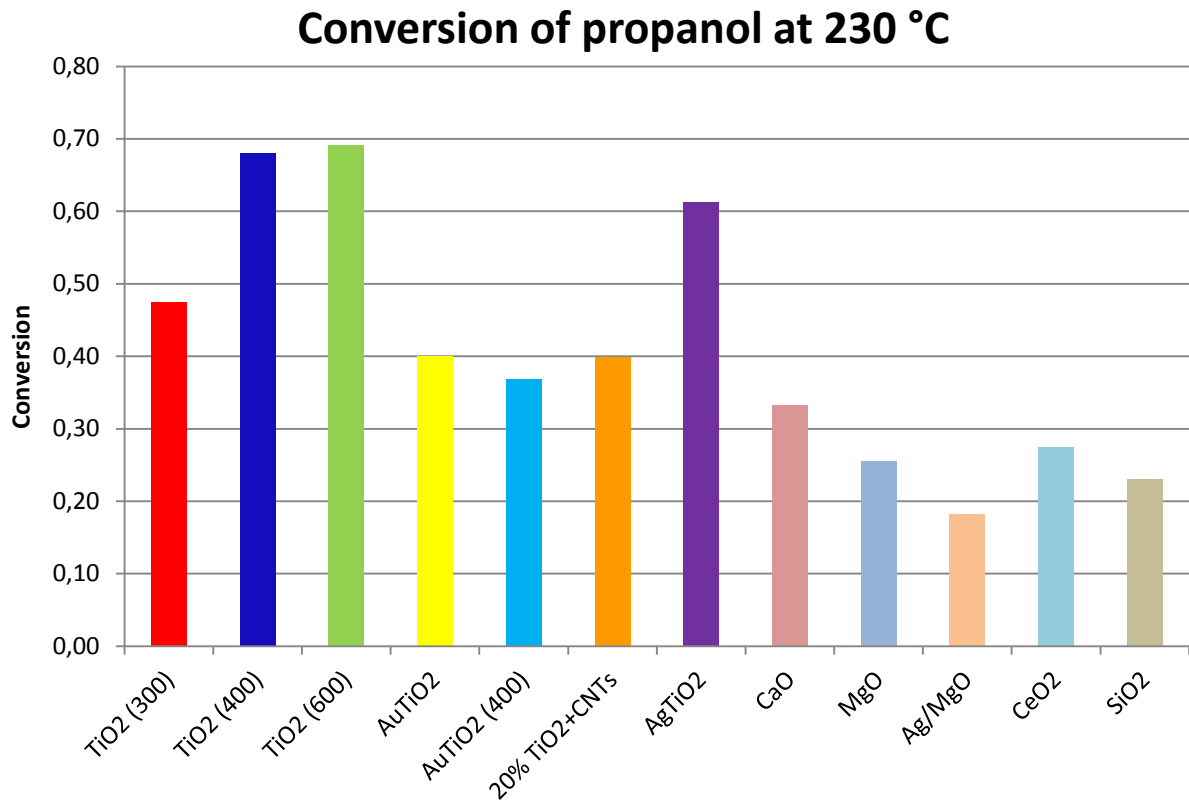
Conversion of propanol at 300 °C
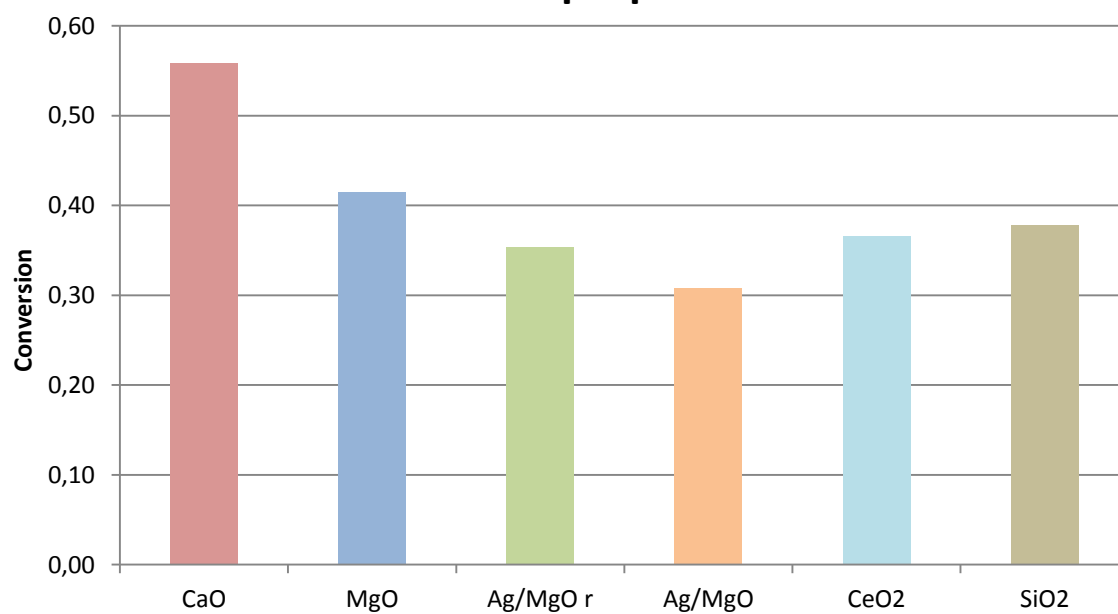
Selectivity to C6 at 230 °C

Selectivity to C6 of TiO2 based catalysts at 300 °C

Selectivity to C6 at 300 °C

Selectivity to C9 at 230 °C

Selectivity to C9 of TiO2 based catalysts at 300 °C
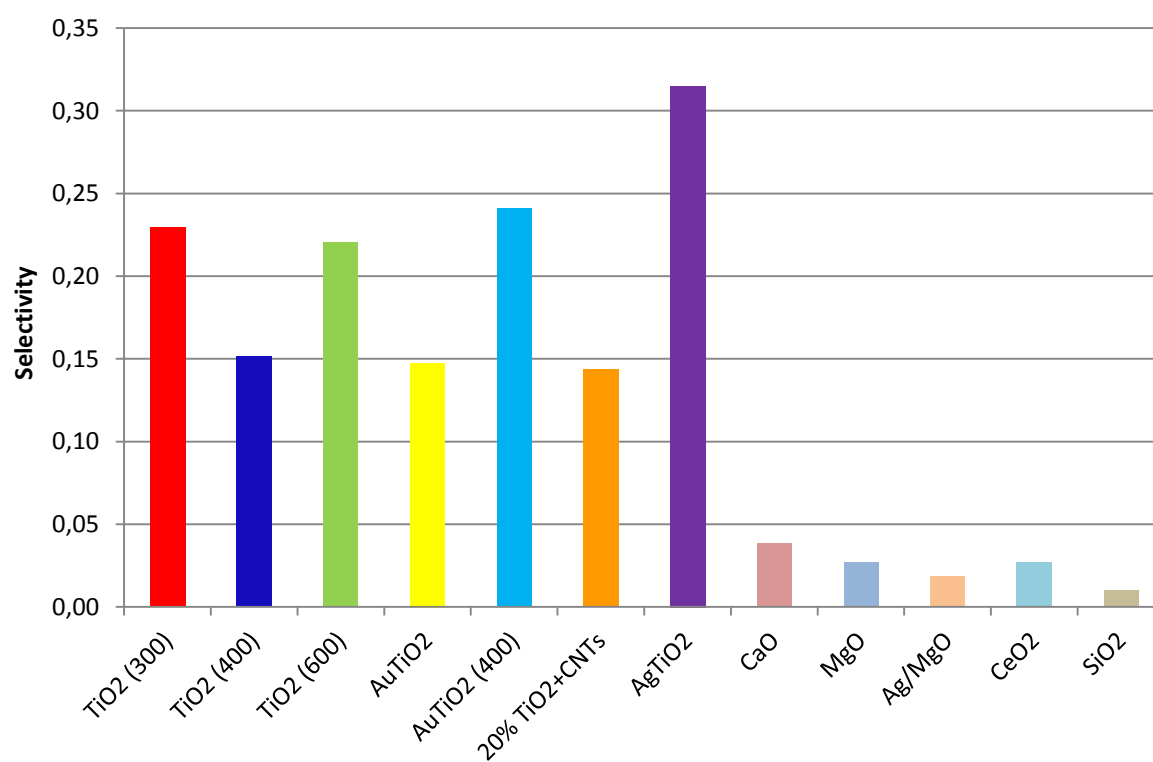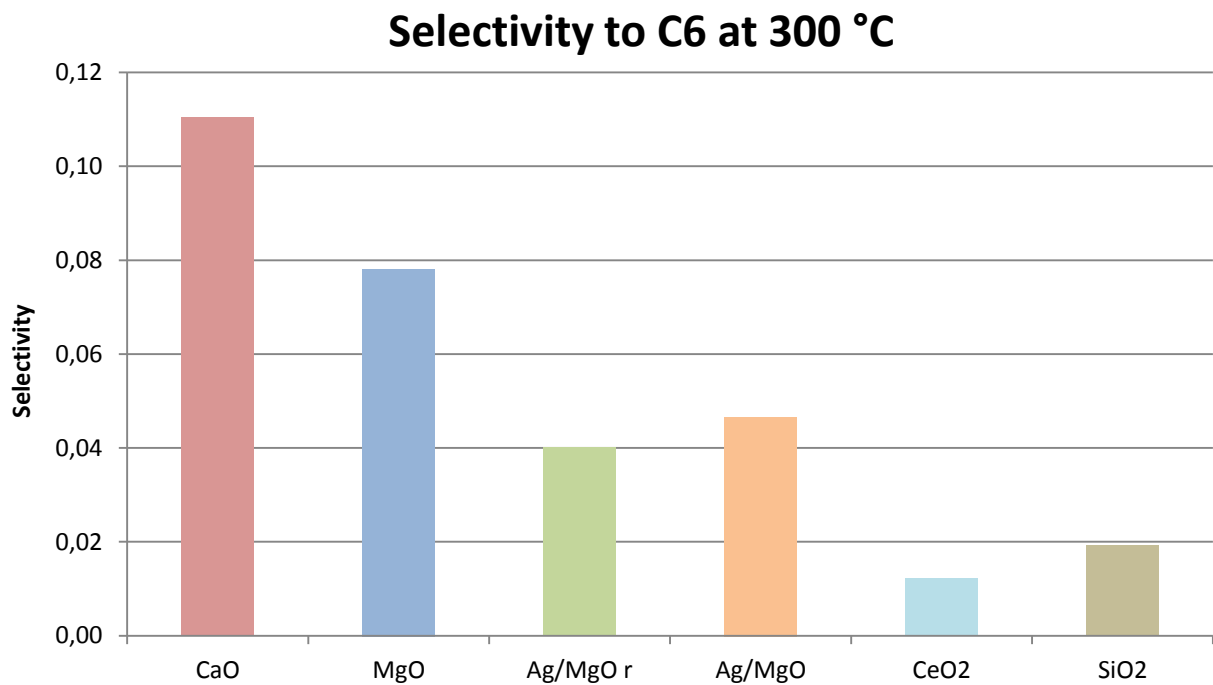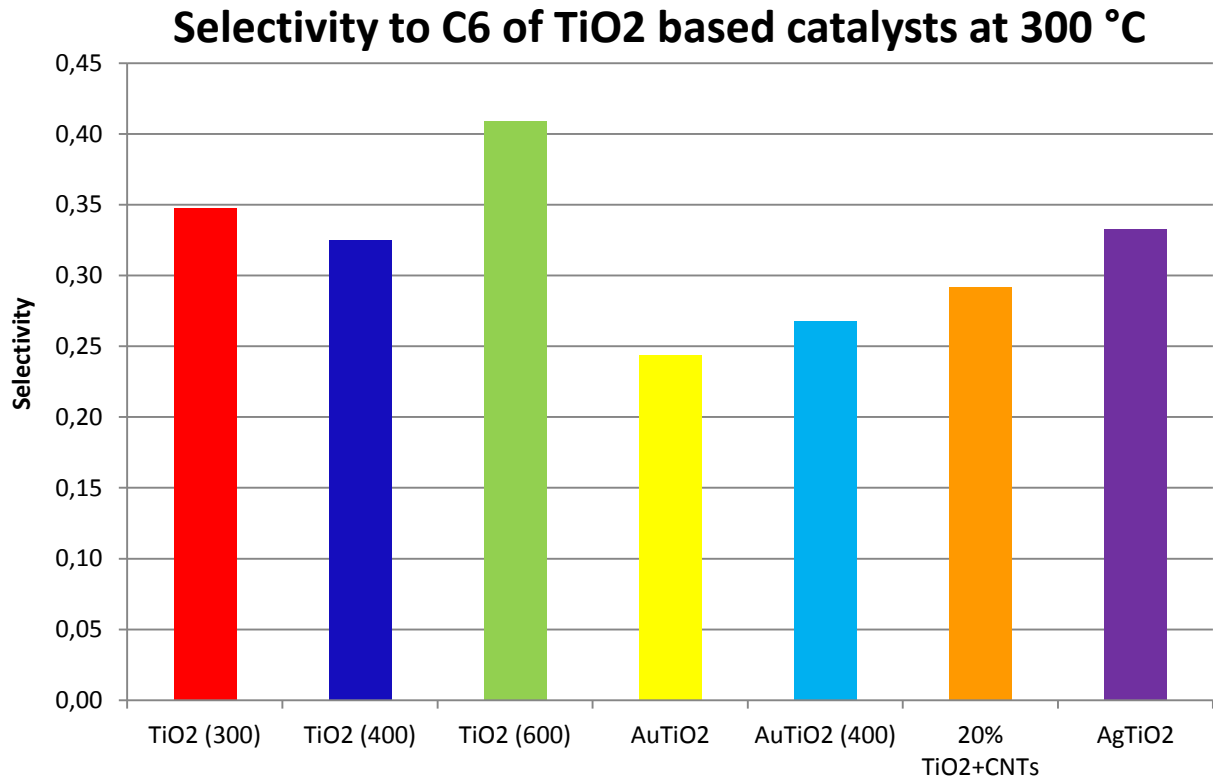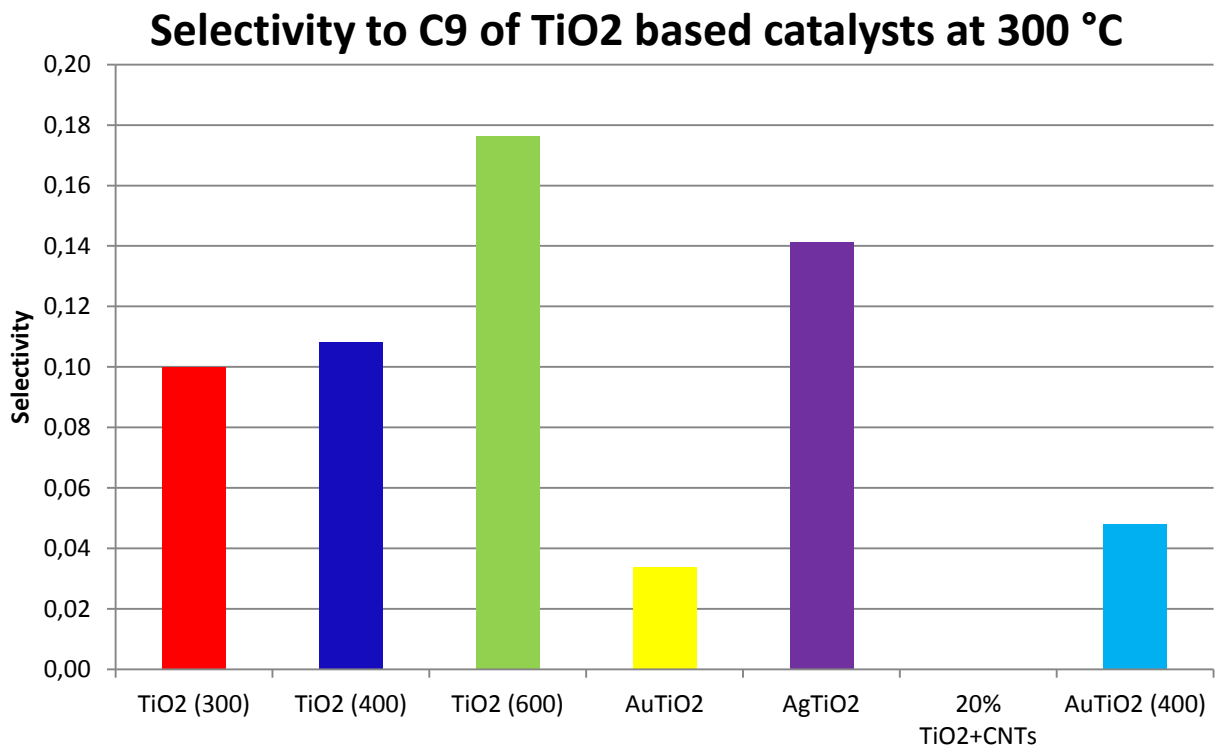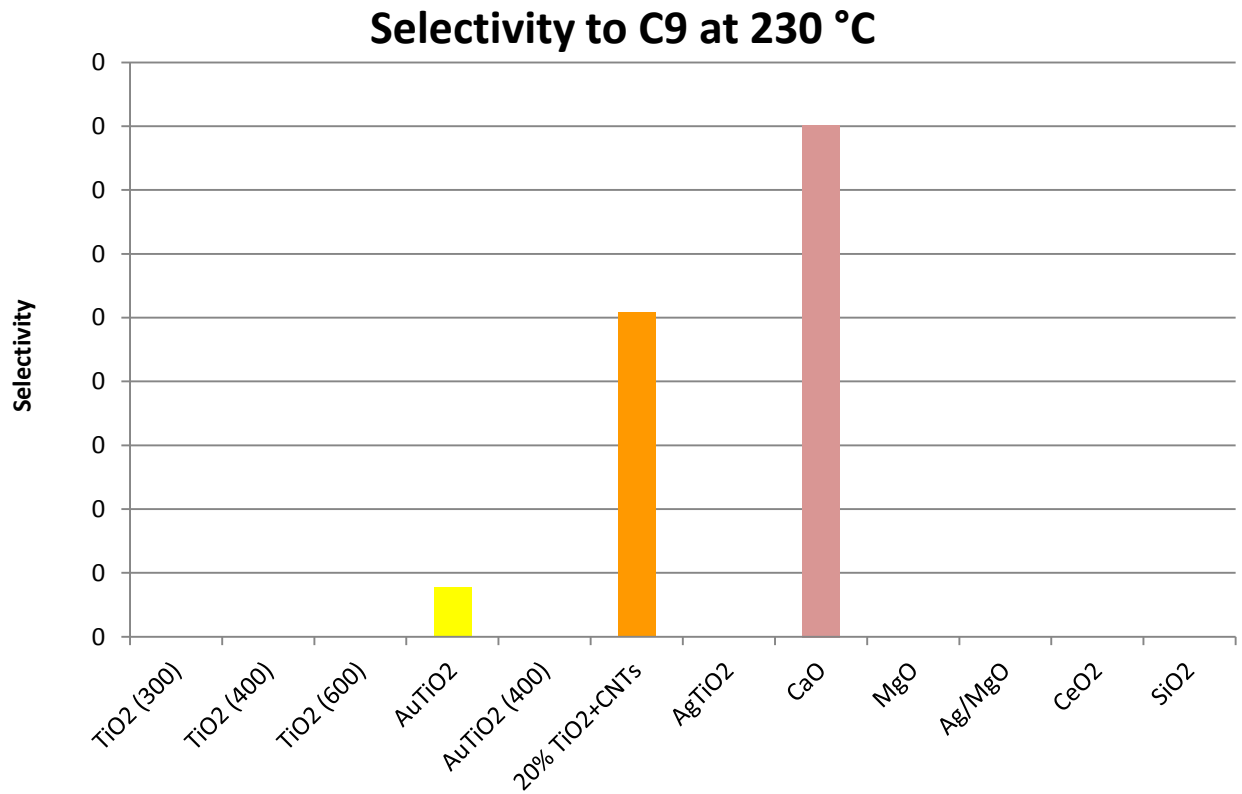
Selectivity to C9 of TiO2 based catalysts at 300 °C
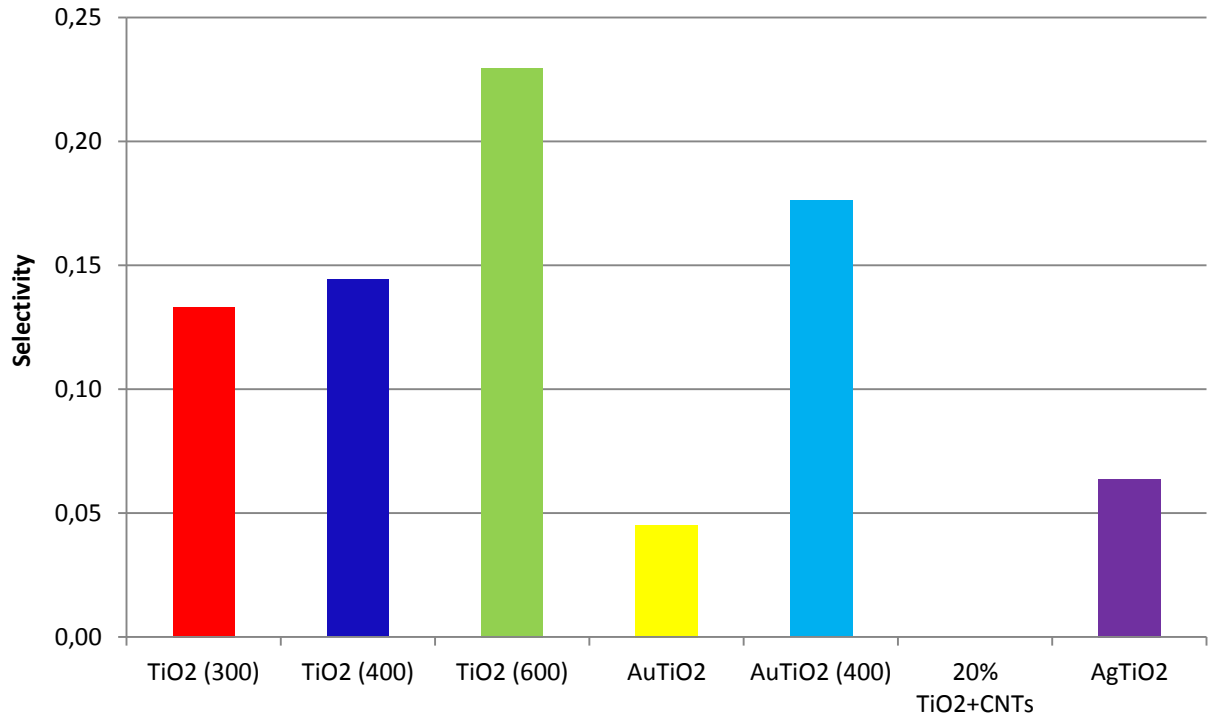
Selectivity to C12 at 230 °C
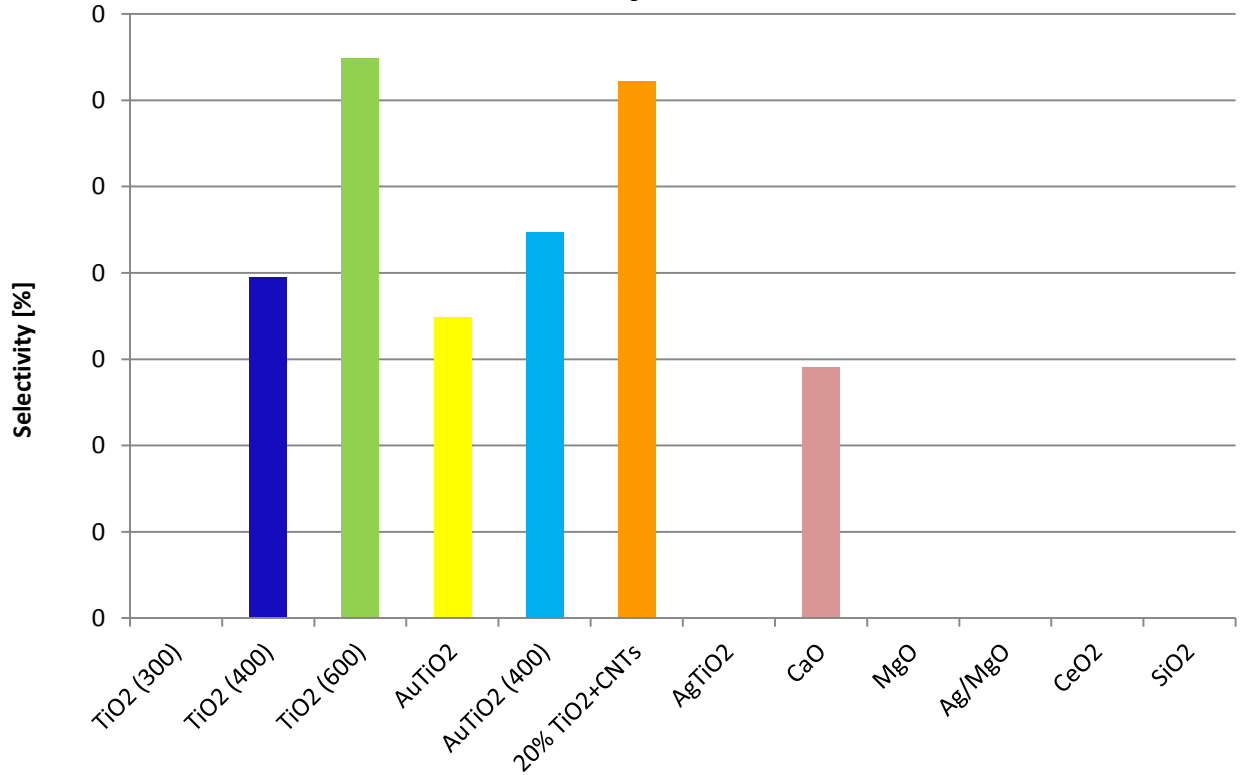
Selectivity to C12 of TiO2 based catalysts at 300 °C
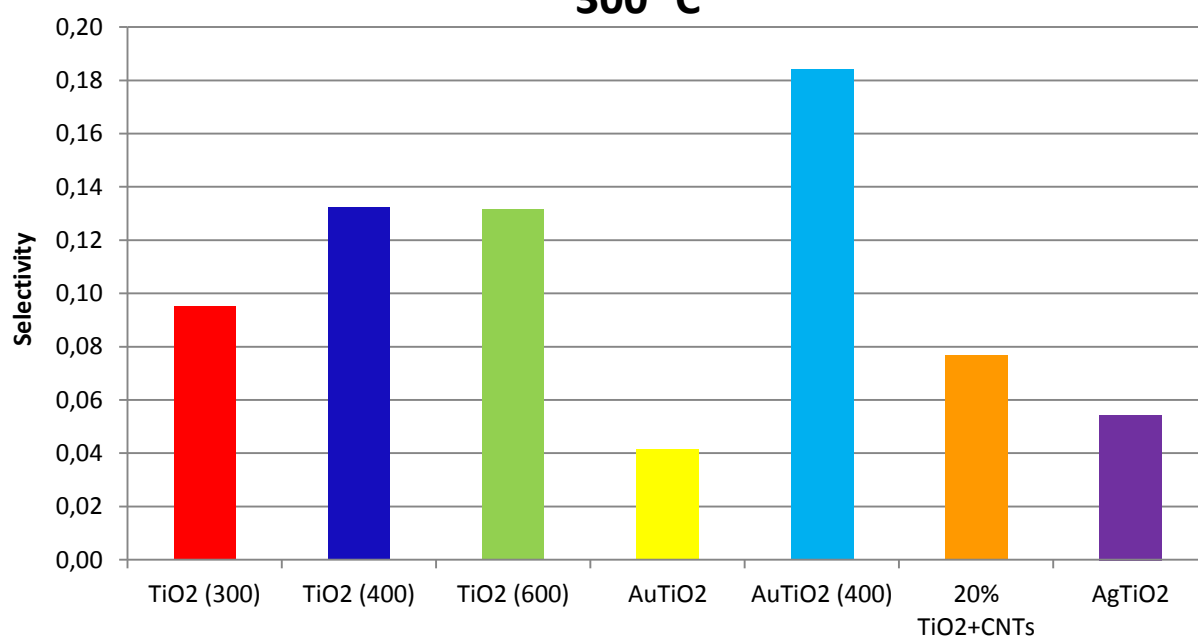
Table 3 - 7 - summary of various properties of each tested catalyst

Catalyst	C3 based conversion	Selectivity			C6 Distribution		
		C6	C9	C12	ketones	aldehydes	alcohols
TiO2 (300)	0,87	0,35	0,13	0,10	0,24	0,05	0,015
TiO2 (400)	0,92	0,32	0,14	0,13	0,19	0,05	0,03
TiO2 (600)	0,88	0,41	0,23	0,13	0,26	0,07	0,03
AuTiO2	0,62	0,24	0,05	0,04	0,19	0,03	0
AgTiO2	0,93	0,27	0,18	0,18	0,15	0,08	0
20% TiO2+CNTs	0,55	0,29	0	0,08	0,17	0,10	0
AuTiO2 (400)	0,49	0,33	0,06	0,05	0,27	0,05	0
CaO	0,56	0,11	0	0	0,055	0,05	0
MgO	0,41	0,08	0	0	0,042	0,04	0
Ag/MgO	0,35	0,04	0	0	0,026	0,01	0
CeO2	0,37	0,01	0	0	0,000	0,01	0
SiO2	0,38	0,02	0	0	0,011	0,01	0
TiO2 (300)	0,47	0,23	0	0	0,17	0,06	0
TiO2 (400)	0,68	0,15	0	0,04	0,11	0,04	0
TiO2 (600)	0,69	0,22	0	0,06	0,15	0,07	0
AuTiO2	0,40	0,15	0,01	0,03	0,12	0,03	0
AuTiO2 (400)	0,37	0,24	0	0,04	0,19	0,05	0
20% TiO2+CNTs	0,40	0,14	0,05	0,06	0,08	0,06	0
AgTiO2	0,61	0,32	0	0	0,23	0,09	0
CaO	0,33	0,04	0,08	0,03	0,01	0,03	0
MgO	0,26	0,03	0	0	0,01	0,01	0
Ag/MgO	0,18	0,02	0	0	0,01	0,01	0
CeO2	0,28	0,03	0	0	0	0,03	0
SiO2	0,23	0,01	0	0	0	0,01	0

Catalyst	ester +ether	HC	alkane	alkene	HC/Oxygenates in whole product		
					HC/ oxygenates	HC	oxygenates
TiO2 (300)	0,015	0,022	0	0,02	0,07	0,25	0,75
TiO2 (400)	0,014	0,04	0	0,04	0,14	0,32	0,68
TiO2 (600)	0,0183	0,03	0	0,03	0,09	0,40	0,60
AuTiO2	0,009	0,02	0	0,02	0,07	0,10	0,90
AgTiO2	0,008	0,03	0	0,03	0,11	0,39	0,61
20% TiO2+CNTs	0,011	0,01	0	0,01	0,04	0,09	0,91
AuTiO2 (400)	0	0,01	0	0,011	0,035	0,13	0,87
CaO	0	0,002	0,000	0,002	0,015	0	1
MgO	0	0	0	0	0	0	1
Ag/MgO	0	0	0	0	0	0	1
CeO2	0	0	0	0	0	0	1
SiO2	0	0	0	0	0	0	1
TiO2 (300)	0	0	0	0	0	0	1
TiO2 (400)	0	0	0	0	0	0,04	0,96
TiO2 (600)	0	0	0	0	0	0,06	0,94
AuTiO2	0	0	0	0	0	0,04	0,96
AuTiO2 (400)	0	0	0	0	0	0,04	0,96
20% TiO2+CNTs	0	0	0	0	0	0,11	0,89
AgTiO2	0	0	0	0	0	0	1
CaO	0	0	0	0	0	0,11	0,89
MgO	0	0	0	0	0	0	1
Ag/MgO	0	0	0	0	0	0	1
CeO2	0	0	0	0	0	0	1
SiO2	0	0	0	0	0	0	1

*HC - hydrocarbons

Catalyst	In whole product				Formation Rate [mmol/g.h]		
	Hydrocarbon/ aldehyde	alkane	alkene	alkane/ alkene	C6 hydro	C6 oxy	C9
TiO2 (300)	0,33	0,09	0,15	0,62	0,09	4,35	1,78
TiO2 (400)	0,46	0,10	0,21	0,45	0,53	3,81	1,92
TiO2 (600)	0,65	0,16	0,22	0,72	0,46	4,99	3,06
AuTiO2	0,11	0,03	0,07	0,36	0,20	3,05	0,60
AgTiO2	0,63	0,13	0,24	0,53	0,35	3,22	2,35
20% TiO2+CNTs	0,10	0,00	0,09	0,00	0,69	19	0
AuTiO2 (400)	0,15	0,04	0,09	0,41	0,15	4,29	0,85
CaO	0	0	0,002	0	0,022	1,45	0
MgO	0	0	0	0	0	1,04	0
Ag/MgO	0	0	0	0	0	0,53	0
CeO2	0	0	0	0	0	0,16	0
SiO2	0	0	0	0	0	0,26	0
TiO2 (300)	0	0	0	0	0	3,06	0
TiO2 (400)	0,04	0	0,04	0	0	2,02	0
TiO2 (600)	0,07	0	0,06	0	0	2,94	0
AuTiO2	0,04	0	0,04	0	0	1,97	0,10
AuTiO2 (400)	0,05	0	0,04	0	0	3,21	0
20% TiO2+CNTs	0,13	0	0,11	0	0	9,57	3,39
AgTiO2	0	0	0	0	0	4,20	0
CaO	0,12	0,03	0,07	0,47	0	0,51	1,07
MgO	0	0	0	0	0	0,36	0
Ag/MgO	0	0	0	0	0	0,24	0
CeO2	0	0	0	0	0	0,36	0
SiO2	0	0	0	0	0	0,14	0

Catalyst	Formation rate [mmol/g.h]			
	C12	R C3-C3	R C6-C3	R C9-C3
TiO2 (300)	1,27	6,77	2,73	1,27
TiO2 (400)	1,76	6,94	3,24	1,76
TiO2 (600)	1,75	8,81	4,38	1,75
AuTiO2	0,55	4,07	1,01	0,55
AgTiO2	2,45	6,98	4,19	2,45
20% TiO2+CNTs	5,11	23,29	3,83	5,11
AuTiO2 (400)	0,72	5,55	1,39	0,72
CaO	0	1,47	0	0
MgO	0	1,04	0	0
Ag/MgO	0	0,62	0	0
CeO2	0	0,16	0	0
SiO2	0	0,26	0	0
TiO2 (300)	0	3,06	0	0
TiO2 (400)	0,53	2,41	0,40	0,53
TiO2 (600)	0,87	3,59	0,65	0,87
AuTiO2	0,47	2,38	0,45	0,47
AuTiO2 (400)	0,60	3,66	0,45	0,60
20% TiO2+CNTs	4,15	14,94	6,50	4,15
AgTiO2	0	4,20	0	0
CaO	0,39	1,52	1,36	0,39
MgO	0	0,36	0	0
Ag/MgO	0	0,24	0	0
CeO2	0	0,36	0	0
SiO2	0	0,14	0	0

4.5.1   Deactivation test

Stability of the TiO$_2$ (600°C), 5 % Ag/TiO$_2$, 5 % Ag/TiO$_2$ (2) catalyst was carried out in the same plug flow reactor as was used for previous experiment although some modification needed to be done to obtain as precise results as possible. From previous experiences, it was known that certain amount of produced liquids was trapped in the condenser. Liquid product was collected every two hours and there was very high chance that some of the liquid residue product trapped in the condenser can contaminate product collected in next run.

To avoid this risk, standard continuously water-cooled condenser was replaced with cold trap. Cold trap consisted of insulated jar cca 35 cm high, glass condenser 30 cm high that was immersed in mixture of acetone and dry ice to obtain temperatures close to -78 °C. Additionally a hollow bronze pipe was included to this cold trap system only to make replacement of condensers easier. During reaction run condenser was replaced every two hours with a new one, to avoid contamination. Moreover, metal pipes form reactor to condenser were designed to be as straight and short as possible to avoid condensation of product along the way. This was done mainly to prevent higher hydrocarbons from condensation. Higher HCs condensate easier than propanol and if the pipeline would not be short and straight it might lead to major looses of product inside the lines. In addition, to maximize amount of collected product pipeline was insulated with the piece of fibreglass to decrease heat loss and condensation along the way. Even more certain solution would be if fibreglass was changed for heating line but then it could cause problems or difficulties with assembling/dissembling of condenser set up, if problem occurs.

Unfortunately, mixture of dry ice and acetone was too cold for this experiment. Very low temperature in the cold trap caused frosting of some liquefied product inside condenser's glass pipe which subsequently led to build up of pressure inside the reactor and sadly also to an accident which followed while the condenser was replaced. Sudden release of pressure, hot liquid and gas made us to re-evaluate the condenser set up. To avoid future risk, dry ice and acetone were replaced by crushed ice and water. We supposed this would reduce risk of frosting inside the tubes, although we were aware it might lead to worse condensation of product in the condenser. However, safety comes always first. This whole accident could have been prevented if pressure sensor would be

included. Sadly when the condenser was modified, modifications on pipeline were done as well and this excluded pathway connecting reactor pipeline to pressure controller and so there was no chance to find out how high pressure inside of the lay out was.

Deactivation test of all three selected catalyst were successfully done and despite the accident, we obtained some relevant data. 5 % Ag/TiO$_2$ catalyst was done twice because of poor performance of prepared 5 % Cu/SiO$_2$ catalyst, which was prepared in the fresh batch. We believe, it was silica support to blame for this failure. When 5 % Cu/SiO$_2$ was prepared again with different support, product composition was as we expected. This shows great importance of 5 % Cu/SiO$_2$ catalyst, which is an essential substance for successful experiment. Copper, as it was mentioned earlier, is there to transform propanol feed into mixture of propanol and propanal, and without any propanal there will be no aldol condensation and hence no successful amount of higher hydrocarbons.

Conversion and selectivity was measured at steady state propanol flow 0,018 g/min for 20 hours, where sample was collected after every 2 hours for 10 hours and then again once after 10 hours. Right after this deactivation test, mass flow of propanol increased from 0,018 g/min to 0,036 g/min, 0,072 g/min, and 0,085 g/min min, respectively. Conversion and selectivity were plotted against time and against propanol flow divided by mass of the catalyst.

Conversion at steady-state conditions (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2 at constant 0,018 g/min of propanol flow)
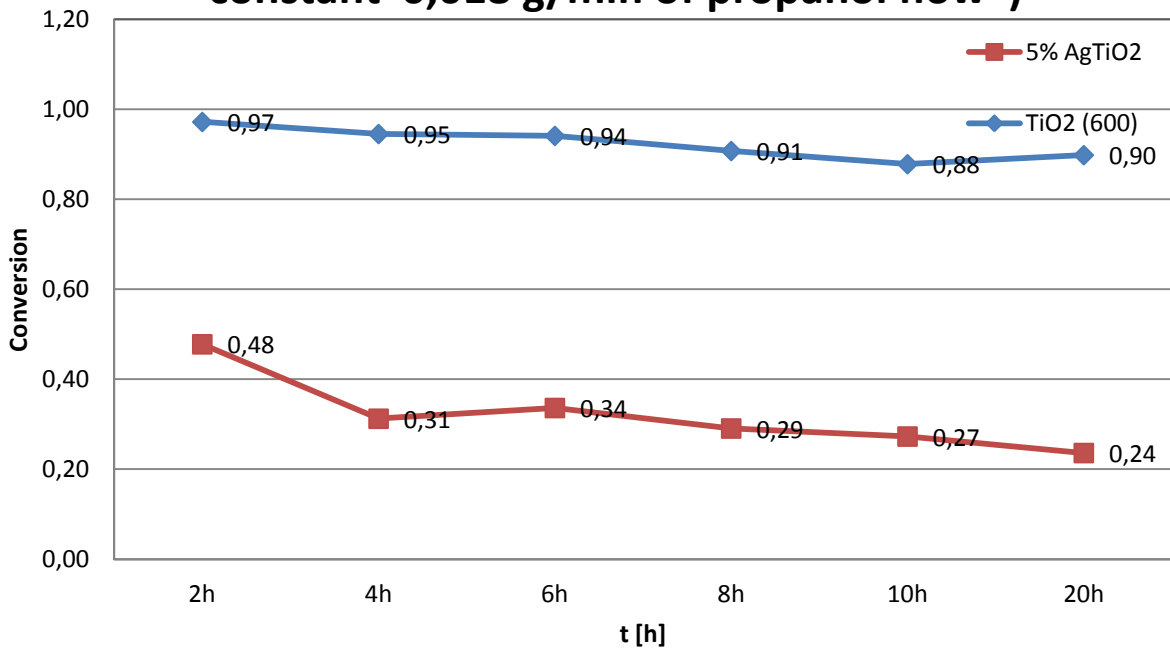
Conversion during incresing flow of propanol, (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2)
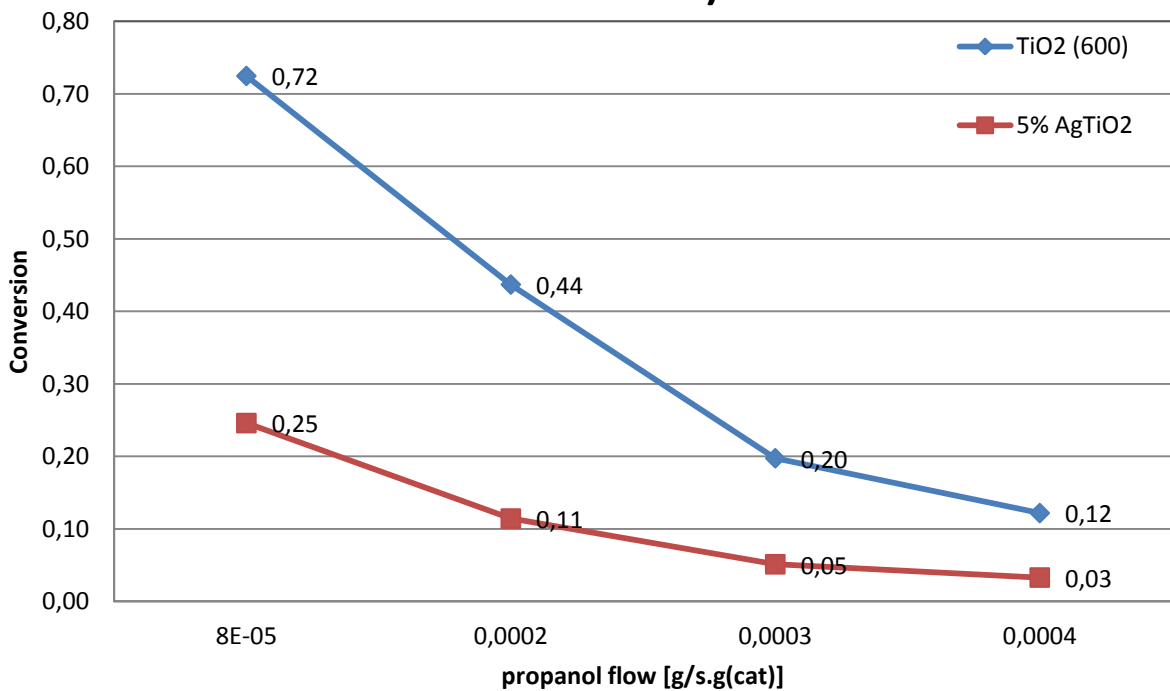
Selectivity of TiO2 at steady state conditions (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2 at constant 0,018 g/min of propanol flow)
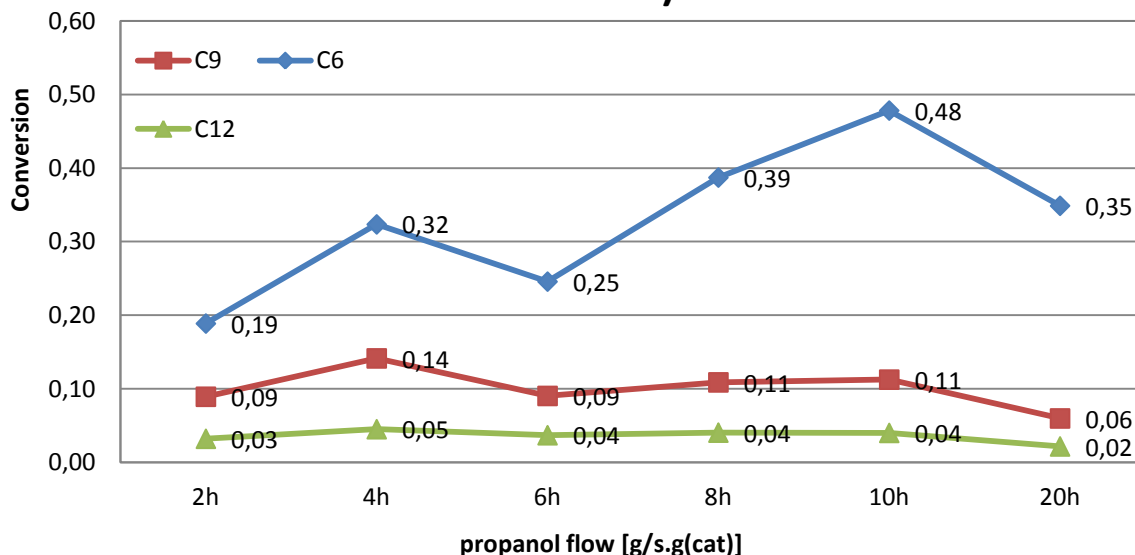
Selectivity of TiO2 during incresing flow of propanol (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2)
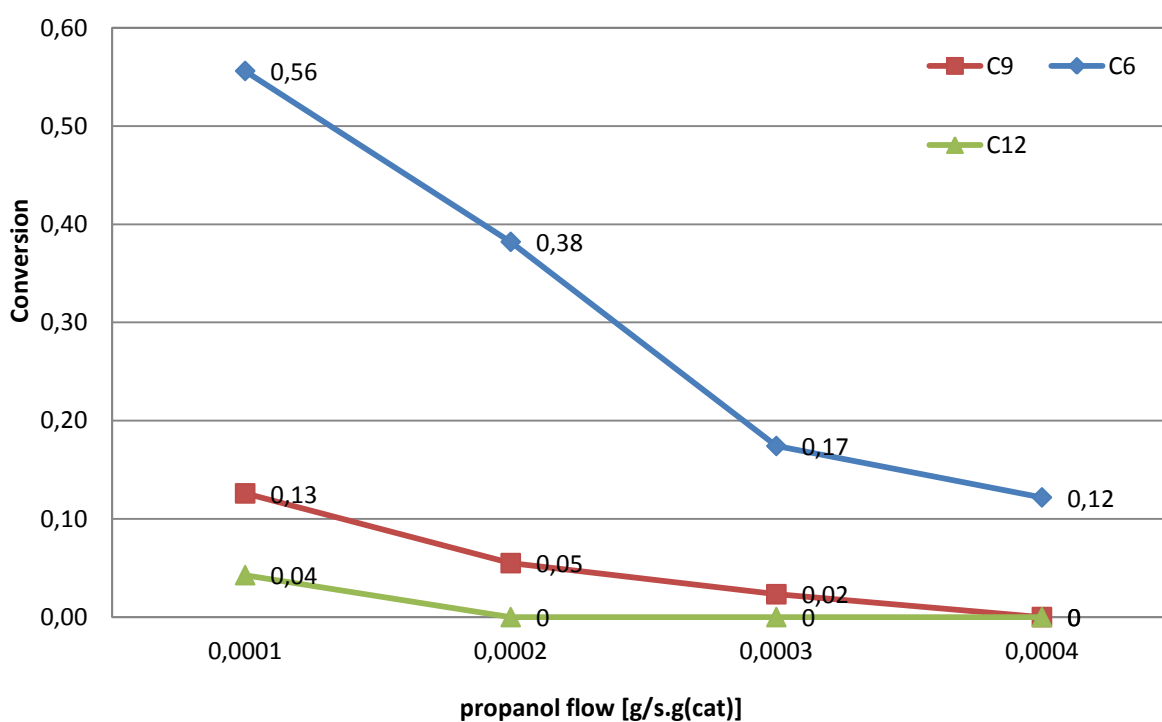
Selectivity of Ag/TiO2 at steady-state (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2)
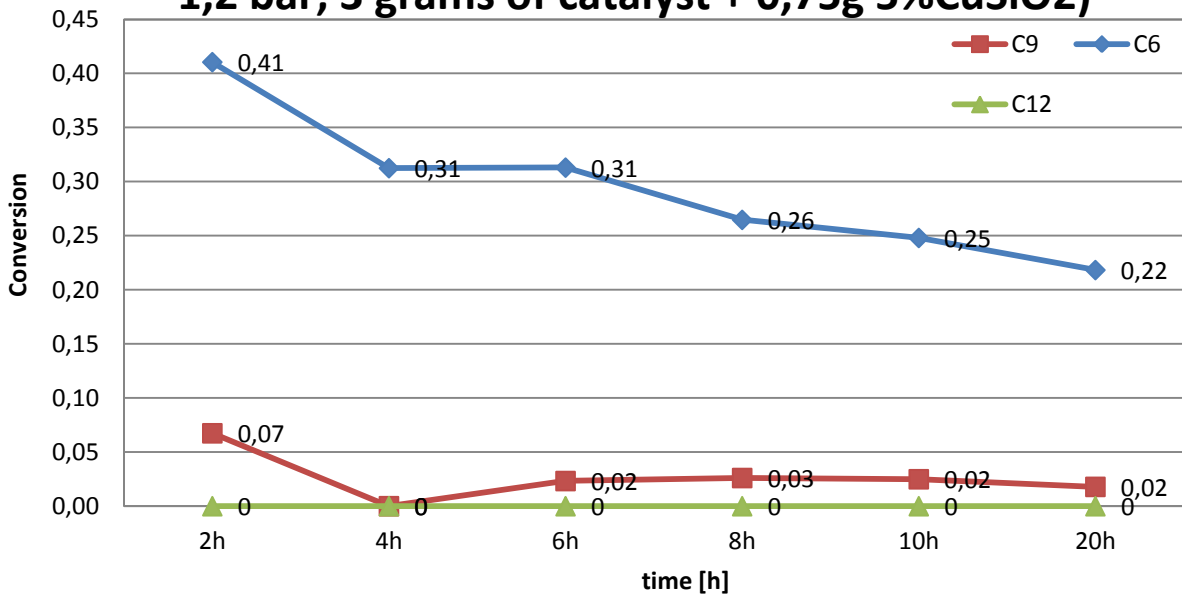
Selectivity of Ag/TiO2 during incresing flow of propanol (3OO °C; 1,2 bar; 3 grams of catalyst + 0,75g 5%CuSiO2)
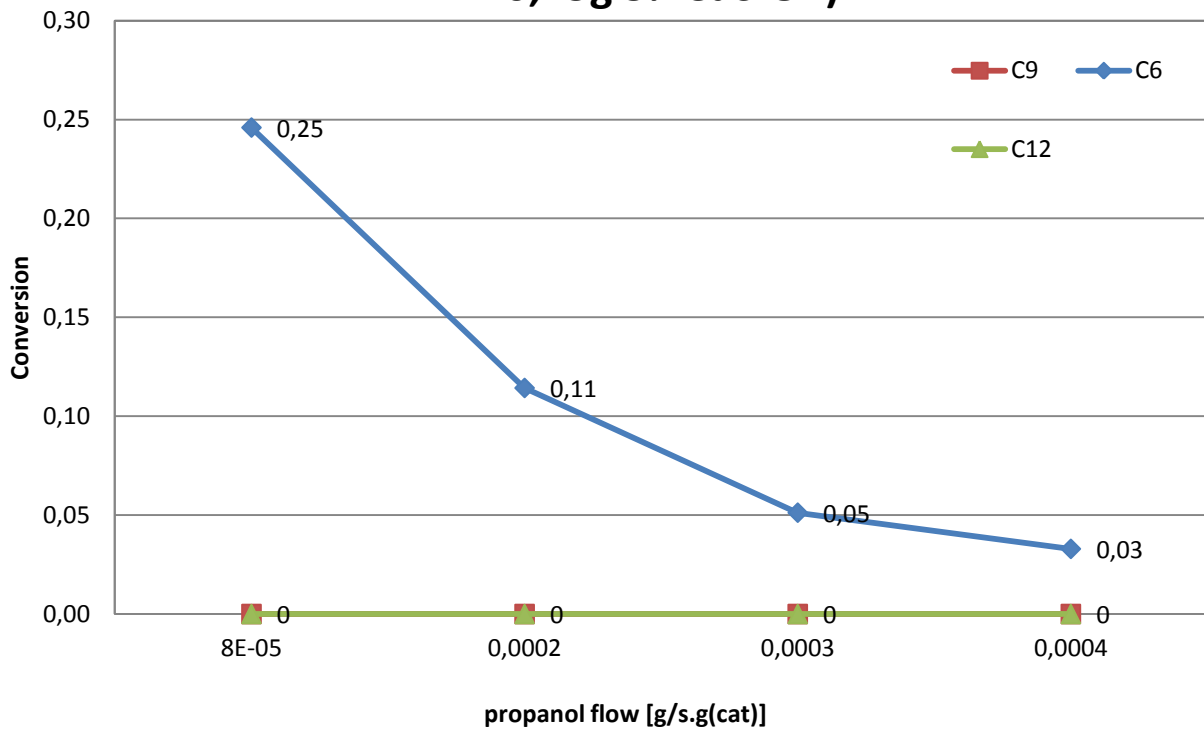
5 Conclusion

Fundamental idea of this project was to find catalyst which will provide highest possible conversion of propanol to C_{6+} hydrocarbons with high selectivity towards desired products. Produced liquid mixture should contain C_{6+} hydrocarbons, aldehydes, ketones and alcohols. Effort is to avoid side reactions which would lead to formation undesired products such as ethers and esters. Results obtained in this work suggest that addition of metal onto the catalyst support does not have to necessarily lead to highest conversion.

Experiments confirmed that from all tested catalysts, titania based catalysts are really the best choice for second step in direct conversion of wooden biomass into liquid fuels. In all cases, they showed highest conversion and highest selectivity towards higher hydrocarbons. We did not successfully confirm that addition of metal onto titania support will improve catalyst performance. In one case addition of silver led to highest measured conversion and it has also high selectivity of higher hydrocarbons, especially then non-oxygenate hydrocarbons. On the other hand, even though 5 % Ag/TiO_2 was prepared in three different batches afterwards, we were not able to reach such a good results again.

However, this was not a failure because main reason for metal addition was to avoid formation of byproducts like ethers and esters. From analysis we received from Statoil, which was a major partner on this project, we can claim that there was no formation of esters and only minor amount of ethers in both products was detected, after reaction on TiO_2 catalyst and of course on 5 % Ag/TiO_2 catalyst. In addition, it was found out that deactivation rate, at least in short testing period (20 hours), for both our catalysts best catalysts was similar and low. Therefore, addition of metal will not drastically change properties of catalyst. This should be good news because preparation of titana catalyst was easy and reproducibility was high, also titania is inexpensive material and without necessity of using noble metal it would be highly economical benefit for the further production.

Nevertheless, area, which should be interesting for future progress, involves carbon nanofibers into the catalyst synthesis. Coating of titania onto carbon fiber led to some interesting results. After closer inspection of our obtained results, 20 % TiO_2 + CNTs could be evaluated as one of the better catalysts even then loading of

titania during the experiment was five times lower compared to other titania based catalysts. Only formation rate was five times multiplied and it is tremendous difference compare to other catalysts. Moreover, synthesis of the catalyst was not complicated and we believe that results would be reproducible.

There was en effort to link performance of our catalyst to theirs basicity. Unfortunately, continuous problems with analyzing device, during this project, make every conclusion uncertain. Nevertheless, it could be said that stronger basic character of catalyst is beneficial for aldol condensation or ketonization. This conclusion is supported by experimental data. From data obtained from TGA before broke down all catalysts with higher basic character except for 5 % Ag/TiO$_2$ performed very good. In addition from obtained data, it could be said that with higher calcination temperature of titania its basic character increased and so its conversion, selectivity and formation rate. Moreover from all non-titania tested catalysts highest conversion were reached with CaO and MgO, which are superbasic catalysts. It is even more interesting considering CaO very low surface area. Our hypothesis, that basic character of the catalyst will improve its performance, is supported by these findings. Although to be more certain, some tests need to be retaken, and tests to find abundance of acid sites should be done in addition to our results.

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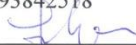
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7 Appendix

• Risk assessment

Operating Instructions

Instrument/Apparatus: Spanish 2			
Serial Number:		Placement:	
Original Manual:			
Log book with signature for training & maintenance: None			

Risk Evaluation
Date: 04.09.2011
Archived:

Compulsory Protection Equipment:		Hazards:	
Safety Goggles	√	Fire	√
Gloves	√	Chemicals/Gasses	√
Hearing Protection		Electricity/Power	√
Protective Clothing	√	Temperature/Pressure	√
Breathing Protection		Cutting/Crushing	
Shielding		Rotating Equipment	
Other		Hazardous Waste	
None		Beyond regular working hours	√
		Others	
		None	

Operating Instructions
1. Load the catalysts in the quaz or steeless reactor;
2. Control the temperature and gas flow from the control panel or computer;
3. Liquid reactants are pressurized by He and introduce to the reactor through evaparator;
4. Gases/products go through the condensor and ventilation;
5. Shut down all gases and cut power after finishing the experiment.
GC manual; HSE - course; leak testing before every experiment.

Emergency Procedure
Shut down gas bottles and cut power, Then evacuate.

Maintenance Routines
Frequency When needed
Service Agreements: None
Maintenance Contact: None
Maintenance Described In Seperate Attachme None outside maintinence.

Equipment Responsible:		Deputy:	
Name: De Chen		Name: Jun Zhu	
Telephone 73593149		Telephone 73594114	
Mobile: 48222428		Mobile: 93842518	
Signature:		Signature:	

Controlled & Updated:
Date:	Date:	Date:
Date:	Date:	Date:

NTNU
Fakultet for naturvitenskap og teknologi

SINTEF
PFI 179

APPARATURKORT
Fakultet for naturvitenskap og teknologi

FYLLES UT MED BLOKKBOKSTAVER AV VEILEDER
(kortet kopieres på gult papir)

FORSØK/APPARATUR: ....Sorption Enhanced 1 (Biomass conversion) Setup..............

STOFF: .... H_2...............................   MENGDE: ...50L.......................................
.... He, N_2.............................   .... 50L, 50L...........................
....

FAREMOMENTER: ....H_2 ---- flammable ....
....Overheating...

MAKS. TID FOR DRIFT UTEN TILSYN: ....Eight hour (leak test needed).......................

BEGRENSINGER I ARBEIDSTID: ....No...

PÅBUDT VERNEUTSTYR: .... Eye protector..

ANDRE VERNETILTAK: ....H_2, CH_4, CO and C_3H_8 detectors ....

ANDRE OPPLYSNINGER: ....
....

HANDLEMÅTE VED NØDSTOPP: ...... ………………………………….....................
.... Turn off the powers in the box, Turn off all the gases................................

VEILEDER: ....De Chen..............TLF.NR.: ....93149.......... SIGN.: ....

APP. ANSVARLIG: .....De Chen...........TLF.NR.: ....93149.........SIGN.: ....

OPERATØR: ....Jun Zhu..............TLF.NR.: .....93842518.... SIGN.: ....

OPERATØR: .... Cesak Ondrej..........TLF.NR.: .... 45170875....SIGN.: ....

GYLDIG FRA DATO: ... Dec.31,2012.................   TIL DATO: ......June 30,2013.............……

side 1 av 2 13.08.2012

NTNU

HMS /KS

Risk assessment

Utarbeidet av	Nummer	Dato
HMS-avd.	HMSRV2603	04.02.2011
Godkjent av	Side	Erstatter
	0	

Unit:
Line manager: *Kjemisk prosessteknologi* **Date:**
Øyvind Gregersen
Participants in the identification process (including their function): 0

Signatures:

ID no.	Activity from the identification process form	Potential undesirable incident/strain	Likelihood (1-5)	Consequence Human (A-E)	Environment (A-E)	Economy/ material (A-E)	Reputation (A-E)	Risk value Human	Comments/status Suggested measures
1	Use of toxic and flammable gases (H2)	Leaks, fire, explosion	2	B				2B	Leak testing with noble gases and room and local detectors
2	Assembling/use of toxic gases CO	Leaks, fire	1	C				1C	Leak testing with noble gases and room and local detectors
3	Assembling/use of non toxic and inert gases: $CO_2/N_2/Ar/He$	Leaks	2	B				2B	Use of gloves, lab coat, gogles.
4	Use of acetone/1-propanol/ethanol as reactants	spill, fire	3	A				2B	Use of gloves, lab coat, gogles.
5									
6									

What's A Risk Matrix

A risk matrix is simple graphical tool. It provides a process for combining the chance for an occurance of an event (likelihood) and the concequence if the event occured. Use the tool for everyday judgements and decisions. Know when to accept the risk. Know when to reject the risk.

Just for information! Do not write in this form.

RISK ASSESSMENT MATRIX

	Column1	Column2	Column3	Column4	Column5	Column6
	Very critical	E1	E2	E3	E4	E5
	Critical	D1	D2	D3	D4	D5
CONSEQUENCE	Dangerous	C1	C2	C3	C4	C5
	Relative safe	B1	B2	B3	B4	B5
	Safe	A1	A2	A3	A4	A5
		Minimal	Low	Medium	High	Very high

Risk Increases In This Direction

LIKELIHOOD

COLOR		Describing function
Red		Extreme risk – immediate action required
Yellow		Attention needed to develop risk reduction strategies.
Green		Minimal injury requiring no/minimal intervention or treatment.

ALARP

Risk will be treated to ensure they are "As Low As Reasonably Practical"(ALARP) or in the "Broadly Acceptable" areas.

Generally Intolerable

ALARP / Tolerable

Broadly Acceptable