

16차 국제 열분해 학회 구두 논문 발표 부분 - 바이오매스 관련 부분만 발췌

## L40. BIOMASS LIQUEFACTION BY FAST OR HYDROTHERMAL PYROLYSIS, A PREPARATION STEP FOR ENTRAINED FLOW GASIFICATION

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Biomass is the only renewable carbon resource for organic chemicals and fuels. At the Karlsruhe research centre a novel process for the conversion of biomass to synfuel is being developed, chemicals and electricity are side products. In the first step, the bulky biomass is liquefied by fast or hydrothermal pyrolysis in a number of decentralised plants. Pulverised chars are suspended in the dense pyrolysis liquors and the resulting slurries are easily transported to a central gasifier for syngas production and use on a larger and more economic scale.

Entrained flow gasification at high temperature (>1000 °C) and high pressure (>50 bar) - more than downstream synthesis - is the central step. Tar-free syngas with low CH<sub>4</sub> content and a molten slag are generated in a few seconds in a flame reaction. Suitable feedstocks are liquids, slurries or any other pumpable liquors with heating values >10 MJ/kg, which can be atomised pneumatically with the substoichiometric amount of oxygen required for gasification. This step has been successfully tested with pyrolysis products from beech wood in a 3 MW pilot gasifier plant at FUTURE ENERGY in Freiberg, Germany.

We are also investigating various biomass liquefaction procedures and liquefied forms in view to their suitability as a preparation step for a pressurised entrained flow gasifier. Special organic wastes and fossil fuels are also considered as a potential feedstock, to qualify a broad feedstock spectrum. In principle, fine powders from biomass or pyrolysis chars with low bulk density are also suited for entrained flow gasification but require inconvenient pressure lock operation. A liquid feed requires less technical effort.

Fast and hydrothermal pyrolysis has been selected as the most promising biomass liquefaction processes. Process development units (PDUs) for studies of both processes with 10 and 20 kg/h biomass throughput, respectively, have been planned and built at Karlsruhe. Design data for both PDUs and first operating experience will be reported.

For the fast pyrolysis of 10 kg/h dry lignocellulosic biomass like straw chops, sawdust etc. a twin-screw mixer reactor is operated in a loop of circulating hot sand as a heat carrier. This twin-screw or LR-(Lurgi-Ruhrgas) mixer reactor has been applied on the technical scale for several decades as "flash coker" for coke and gas production from coal, as "sand cracker" for olefin production from naphtha or for oil recovery from tar sand and vacuum residue. If this reactor type is also suited to produce high condensate yields from biomass pyrolysis vapours, scale-up is not expected to present many problems.

A hydrothermal reactor for the conversion of ~20 kg/h (DOM) wet biomass with up to 100 kg/h water has been built and operated for direct biomass gasification at supercritical conditions of ~300 bar and up to 700 °C, using special construction materials. The facility will also be operated at subcritical conditions at 300-350 °C for hydrothermal conversion of biomass, generating a liquid form with varying melting points up to about 100+ °C.

Use of pyrolysis liquors as direct liquid fuel e.g. for burners or combustion engines, usually requires pure liquids, careful preparation, handling and upgrading. So far no commercial biomass liquefaction facilities are in operation. The quality requirements for gasification are considerably lower; purity and solids or ash content are without much importance. It is therefore expected, that the biomass liquefaction procedures can be considerably simplified. Simpler and cheaper processes may contribute to a commercial breakthrough of fast and hydrothermal pyrolysis.

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## L41. THE EFFECT OF WATER AS REACTION MEDIUM IN CLOSED VESSEL PYROLYSIS OF BIOMASS

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The need for renewable transport fuels has been highlighted through the recent European policies for rapid increase of the contribution of non-fossil components in motor fuels. For pyrolysis liquids this is a challenge, as the pyrolysis liquids from the most developed technologies are not suitable for use in standard motors. However, the composition of liquids produced by biomass pyrolysis is strongly influenced by the reaction conditions, and choice of technology and design of the experimental conditions can change the chemical composition of the fluids to a very large degree [1]. In this work, we have optimised the closed pyrolysis of two biomass types so as to produce a maximum amount of potential fuels using factorial experimental designs. The inputs are a potential energy crop, Reed Canary grass, and an alkaline aqueous waste stream from fine paper production termed Alkacell. The aim is to maximise the yield of petroleum compatible liquid products by finding an optimal combination of temperature, duration, amount of water present and addition of alkali. The gaseous, organic, aqueous and solid fractions have been quantified and analysed by standard protocols for petroleum characterisation, and the fluid fractions have been subjected to detailed molecular analysis.

As shown in Figure 1 (Reed canary grass) and Figure 2 (Alkacell), the distribution of the products between the fractions is very dependent on the reaction conditions (given in Table 1). For both systems, increasing the amount of water relative to biomass increases the liquid yield, and reduces the coke and high molecular weight asphaltene (tar) fraction. The Reed Canary grass requires addition of a base (NaOH, 1-2 M solution) to maximise liquid yields. In the aqueous medium, gas generation is suppressed, while the low molecular, hydrogen rich products are increased. Major product fractions are the aqueous carboxylic acids and phenolic compounds in the organic liquids. Some hydrocarbons are formed, possibly by a "one-pot" Fischer-Tropsch type reaction. Water as a reaction medium increases the yield of stable liquid products with low molecular weight, and makes the organic liquid product more petroleum compatible. The presence of water in the system increases the hydrogen content of the product, and decreases oxygen content. A major part of the liquids produced are not water soluble, so an organic phase is easily separated out. The aqueous products, typically acetic acid, can be recovered by standard industrial methods. These products have a potential for conversion into fuel components with moderate refining. However, perhaps the simplest way to contribute to increased use of renewables would be to substitute biomass derived fractions like phenols for petroleum derived chemicals.

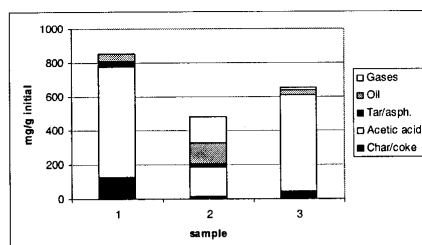


Figure 1: Some product slates from Reed Canary grass

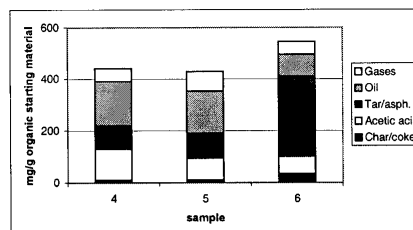


Figure 2: Some product slates from Alkacell

Table 1: Experimental conditions for selected experiments (in a 71 ml ss reactor or \*: 21 ml ss reactor)

	Temp.	Duration	Alkali	Volume aq.	Biom. load.		Temp.	Duration	Volume	Org.load
	Deg. C	hours	moles/L	ml	grams		Deg. C	hours	ml	grams
Sample 1:	360	6	1	9	0.05	Sample 4:	330	17	* 10.7	1
Sample 2:	390	18	2	20.5	3.03	Sample 5:	330	7	31.6	1.9
Sample 3:	360	18	2	20.5	1.05	Sample 6:	330	2	* 12	3.7

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## **L42. PYROLYSIS OF BIOMASS AND WASTE; ROBUST PRE-TREATMENT FOR FUEL CELL APPLICATION**

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The use of waste and biomass for energy production contributes substantially in reduction of CO<sub>2</sub> emissions. For the conversion of waste to energy, incineration is considered as state-of-the-art technology. Staged gasification (low temperature pyrolysis and high temperature gasification) in combination with pyrometallurgical smelting however offers principal advantages with respect to energy efficiency and secondary products. Products are synthesis or fuel gas (for combined heat and power), metals/metal mixtures (for recycling) and construction material (synthetic basalt). Advantages of the combination of gasification with smelting compared to incineration are efficient and cheaper fuel gas cleaning (less emissions) and synthetic basalt as high quality secondary product. High input flexibility is obtained with the low temperature (approx. 500 °C) pyrolysis step. Waste and biomass can be rather inhomogeneous and can include, amongst others, plastics, metals and minerals. Direct gasification is difficult because of the necessary pre-treatment and potential slagging and fouling problems. Pyrolysis is a very robust 'pre-treatment' step converting the inhomogeneous input in tar rich gas and char. The tar rich gas is converted in syngas in the high temperature gasifier, while the char is used as the necessary energy source for smelting of the metals and minerals into basalt. Decentralised operation with this commercially available technology is feasible using a wide variety of (local) non-recyclable wastes like automotive shredder residue (ASR), construction and demolition waste (C&D), contaminated biomass, electronic scrap, and sludges. Overall electrical efficiency of up to 35% is possible applying gas engines with waste heat recovery. As the fuel gas is rich in hydrogen and carbon monoxide it is also applicable for especially high temperature fuel cells like the solid oxide fuel cell (SOFC). The SOFC is very suitable as it can convert both hydrogen and carbon monoxide.

An assessment study was performed for the combination of low temperature pyrolysis, high temperature gasification, pyrometallurgical smelting and SOFC. Based on pyrolysis tests in the ECN bench-scale facility Pyromaat with waste and biomass, mass and energy balance calculation were performed using Aspen<sup>PLUS</sup>. It was calculated that when applying SOFC the overall electrical efficiency for waste to energy increases up to 40-50%. This paper describes the results of the assessment study and the bench-scale pyrolysis tests.

### **Keywords**

Biomass, waste, pyrolysis, gasification, fuel cells

### L43. USING PISTACHIO SHELL AS A RENEWABLE ENERGY SOURCE TO PRODUCE HIGH QUALITY BIO-OIL AND CHAR

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The disposal of solid wastes such as biomass, industrial and municipal wastes is one of the main problems of the world and it is necessary to find out new ways to reuse this great potential as raw materials to produce advantageous products. Pyrolysis of biomass seems to be an appropriate method since it simply gives solid, liquid and gaseous products yields and compositions of which depend on pyrolysis conditions [1-3].

In this study pistachio shell is taken as the biomass sample to investigate the effects of pyrolysis temperature on the product yields and composition. Slow pyrolysis of pistachio shell having an average particle size of 1.82 mm in a fixed-bed reactor at atmospheric pressure was held out to the temperatures of 300, 400, 500, 550, 700°C with a heating rate of 7°C/min. As seen in figure 1, maximum liquid yield was attained at about 500-550°C pyrolysis temperature with a yield of 20.5 %. Elemental analysis was applied to bio-oil to calculate its calorific value. The liquid product obtained under this optimum temperature was fractionated into aliphatic, aromatic and polar subfractions using column chromatography. The aliphatic subfraction was then analysed by GC/MS. For further structural analysis FT-IR spectra of bio-oil and its subfractions were taken. The chemical characterisation has shown that the oil obtained from pistachio shell may be potentially valuable as fuel and chemical feedstocks.

Solid product, char, has also a great potential to be used as a solid fuel or as activated carbons. To identify the properties of solid product proximate and elemental analysis were applied and results of elemental analysis are given in Figure 2. Also calorific values of the chars were determined. It is found that the increase in pyrolysis temperature led to an increase in ash content of the char and a decrease in volatile matter content. FTIR spectra of the chars obtained under different temperatures were also taken to investigate the functional groups.

Key words: pistachio shell, biomass pyrolysis, bio-oil characterization, char characterisation

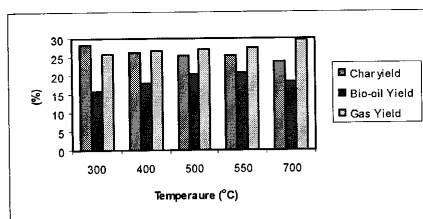


Figure 1. Pyrolysis product yields

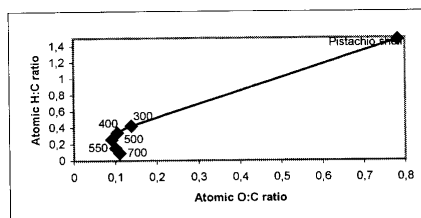


Figure 2. Van Krevelen diagram for chars obtained at different temperatures (°C)

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char  
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## L46. CATALYTIC PYROLYSIS OF EUPHORBIA RIGIDA IN THE WATER VAPOUR ATMOSPHERE

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Nowadays, world energy consumption increases as a parallel with population rise and technology. According to the researchers existence of petroleum 45 years, natural gas 65 years and coal 240 years. The diminishing trend of the this primary sources and the environmental problems caused by these sources have prompt us to investigate other alternative renewable sources of liquid hydrocarbons. Biomass is an important energy source, not only it is renewable, but also it doesn't cause green139house effect, it is abundant, cheap, and it gives synthetic fuels and very important chemicals. In this study, *Euphorbia rigida*, which grows in large quantities in arid lands like many regions in central Anatolia, was considered as candidate for potential renewable energy source. Also *Euphorbia rigida* is characterised by its ability to produce a milky latex and emulsion of about 30% w/w terpenoids in water. The economics of biomass pyrolysis are generally considered to be most favourable for plants, which grow abundantly and require little cultivation in arid lands. In this study Co-Mo commercial catalyst (Criterion-534) was used.

In the experimental studies, firstly the raw material was analysed for its moisture, ash, volatile matter, fixed carbon and raw cellulose. The elemental composition was determined by elemental analysis. Then experiments were carried out in water vapour atmosphere in a fixed-bed Heinze reactor with a heating rate of 7°C/min, pyrolysis temperature of 550°C and mean particular size of 0.55 mm by mixing the catalyst to feedstock in different percentages. Experiments were carried out with the catalyst ratio of 5, 10, 20, and 25 (weight%) under water vapour with the velocities of 0.6, 1.3 and 2.7 cm/s to determine the effect of catalyst and water vapour on the product yields and bio-oil composition. The bio-oil increased to a value of 42.56% when using catalyst ratio of 20% and water vapour flow rate of 1.3 cm/s.

Pyrolysis oils were examined by using elemental analysis, IR and <sup>1</sup>H-NMR spectroscopy. The liquid products were also fractionated by column chromatography. The spectroscopic and chromatographic analysis of the fractions including the gas chromatographic analysis of n-pentane eluates was performed.

According to the results obtained in this study, it is possible to produce petroleum-like liquid pyrolysis products by catalytic pyrolysis of *Euphorbia rigida* in the water vapour atmosphere as an alternative energy source.

## L47. EFFECT OF MANGANESE BASED PIGMENT CATALYST ON THE CO REMOVAL DURING BIOMASS PYROLYSIS

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Commercially available manganese based black pigment was evaluated for its potential as a CO oxidation catalyst. During laboratory test of pure catalyst with 4%CO-21%O<sub>2</sub>-He gas mixture the catalyst oxidized 100% of the CO to CO<sub>2</sub>. However, the performance of a CO catalyst in laboratory test under ideal conditions is not always transferable to the real pyrolysis conditions where other pyrolysis products could hinder the catalyst performance. In this study, the effects of the black pigment catalyst on CO removal during the pyrolysis of catalyst-tobacco system were evaluated in inert and oxidizing conditions.

The experiments were carried out in a flow tube reactor connected to a multi-gas analyzer capable of measuring CO, CO<sub>2</sub> and O<sub>2</sub> concentrations. Pyrolysis experiments were also carried out using a TG/DSC system connected to a quadrupole mass spectrometer to identify the gaseous species and correlate their evolution with heat release profiles. Materials were characterized by X-ray powder diffraction and scanning electron microscopy which revealed existence of mixed oxides (Cu<sub>1.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>-Mn<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub>) in the black pigment with the average particle size of 30-300nm. Experimental results showed that presence of catalyst did not affect the pyrolysis of biomass/catalyst mixture in an inert atmosphere. However, the results of pyrolysis in the presence of oxygen (21% O<sub>2</sub>-He) showed significant effect of catalyst as the amount of CO production in presence of catalyst was reduced by 56%. In addition, ignition of the biomass/catalyst mixture started at a lower temperature of 260°C as opposed to a higher ignition temperature of 300°C of pure biomass. TG/DSC experiments showed evidence of two stage oxygen consumption at 320°C and 430°C during pyrolysis of biomass/catalyst system while oxygen consumption occurs only once at 430°C in case of pure biomass pyrolysis. Based on the experimental findings a mechanism of reaction was proposed. The results show that manganese based mixed oxide catalyst is a promising CO oxidation catalyst for biomass pyrolysis.

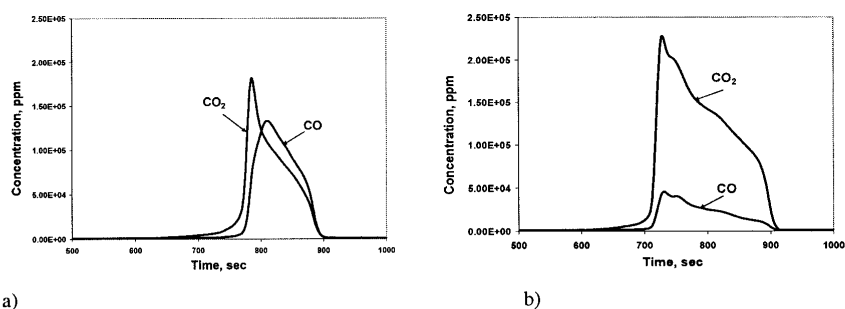


Figure 1. CO and CO<sub>2</sub> concentration profiles during pyrolysis in 21% O<sub>2</sub> up to 500C; a) tobacco only, b) tobacco/catalyst mixture.