

## PYROLYSIS AND HYDROLYSIS OF BIOMASS AND LIGNINS - ACTIVITIES AT THE INSTITUTE OF WOOD CHEMISTRY IN HAMBURG, GERMANY

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### INTRODUCTION

After the first oil price crisis in 1973 research activities were initiated throughout the world to produce oil from renewable feedstocks like lignocellulosic biomass. Countries with huge biomass resources and strong dependence on imported petroleum such as Canada and the United States of America were leading in research at that time. At the Pittsburgh Energy Research Center (PERC) high pressure liquefaction of cellulosic wastes was studied using carbon monoxide and sodium carbonate as a catalyst (1), and a pilot plant in Albany, Oregon was constructed. At the same time, another high pressure conversion process for woody biomass was investigated at the Lawrence Berkeley Laboratories (2). The scaled-up version of this process was also tested in Albany. After several years of operation, the pilot plant was shut down due to economical and technical reasons. It was felt that high pressure technology is too sophisticated for the thermal conversion of biomass into liquid fuels and that simpler technologies should be developed. Therefore, in 1980 the Solar Energy Research Institute (today NREL) in Golden, Colorado, organized a specialists' workshop on fast pyrolysis of biomass. This process promised to give high yields of liquid products. During the workshop, researchers working on coal and biomass presented papers on both fundamental aspects - such as heat transfer mechanisms - and practical work regarding process parameters such as feedstock, particle size, heating rate, residence time, pressure etc. Since the early eighties a lot of progress has been made in the development of conversion technologies for biomass. The most important processes with their characteristics are compiled in Table 1.

In 1982 the German government also recognized the need for using renewable feedstocks and funded a research project dealing with the direct conversion of wood into a liquid fuel and/or chemical feedstocks. Based on the large tradition and experiences in coal conversion by the high pressure Bergius-Pier process in Germany (14 plants produced all transportation fuels during World War II) the Institute of Wood Chemistry (IWC) adopted the process principles to woody feedstocks. During several years of experimental work at IWC, various process alternatives were studied covering

- slurry phase hydrocracking in batch and semi-continuous reactors
- hydrolysis in batch and semi-continuous reactors
- flash pyrolysis in a bench-scale fluidized bed reactor.

In the present paper the research activities and main results on thermochemical conversion of biomass and lignins are summarized.

### HIGH PRESSURE EXPERIMENTS

Initial hydrocracking experiments were conducted in 25 ml autoclaves to compare conversion rates of different lignocellulosic feedstocks and to develop methods for separation and chemical characterization of the liquids (3, 4). Palladium on active charcoal (Pd/C) was initially used as a catalyst. Temperature was 475°C and initial hydrogen pressure 6 Mpa. Surprisingly, very small amounts of solid residue ranging from 0.5 to 6.8 % were observed for all kinds of biomass such as softwood, hardwood, straw, sugar cane bagasse, lignins and cellulose. The oil

yields of the lignocelluloses were in the range of 41 %. Cellulose and hemicelluloses gave rise to around 30 % and lignins to ca. 62 % of an oil. The average molecular weight of the oil was around 500 Dalton indicating severe depolymerization of the feedstocks during hydrocracking. The mass balance of these studies demonstrated that lignin is a more suitable feedstock with respect to oil yields than cellulose and hemicelluloses which have a tendency to give more char, water and gas.

After these orienting studies with the micro-autoclaves, experimental work was continued including a 1-L autoclave system (see Figure 1).

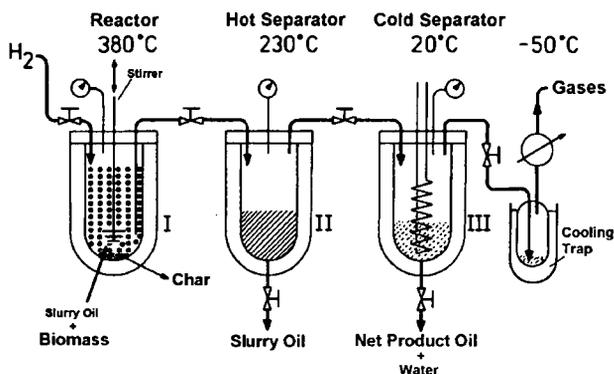


Fig. 1-L autoclave system for hydrocracking of biomass

It consists of a high pressure stirred reactor, a high pressure hot separator and a high pressure cold separator (5). A slurry phase catalytic hydrocracking process was developed with Pd/C as catalyst. In general, spruce wood particles were mixed with the high boiling recycle oil fraction which was condensed in the hot separator at 230 °C. The light and middle distillate fraction was collected in the cold separator and yielded around 37 % of a net product oil (NPO). Several consecutive runs were made in which always the hot separator fraction of the previous run was used as a slurry oil. In this way, the stability of the recycled oil was proved and the conditions of a continuous process could be simulated. The experiments revealed that the NPO yields and the amount of recovered recycle oil were almost constant in all runs. Therefore, a mass balance was established which reflects the overall yields of each product fraction from hydrocracking of biomass (Figure 2).

Beside palladium, other catalysts were included in the hydrocracking experiments such as Co, Mo, Cr, Ni, Fe, and red mud. However, none of these catalysts reached the NPO yields of palladium. The slurry oil could be completely recycled only in the presence of the iron catalyst and a NPO yield of 28 % was found. In general, the NPO's had a heating value of around 37 MJ/kg. An energy balance for the hydrocracking conversion process is presented in Figure 3, taking into account a hydrogen consumption of 4 % and the individual proportions and heating values of the biomass constituents. The balance demonstrates that 59 % of the input energy can be recovered and concentrated in the NPO. Its light fraction amounted to 50 % having a boiling point range < 220°C. The rest could be completely distilled between 220-360°C. In

comparison to oils obtained in the Albany plant, the NPO had a very low viscosity of 3.88 cSt at 20°C, a low pour point of -24°C, and a low density of 0.92 g/l (6).

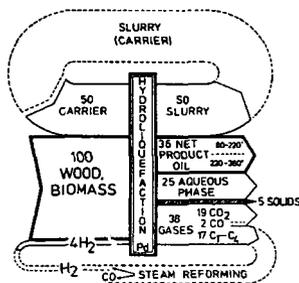


Figure 2 Mass balance for hydrocracking of biomass

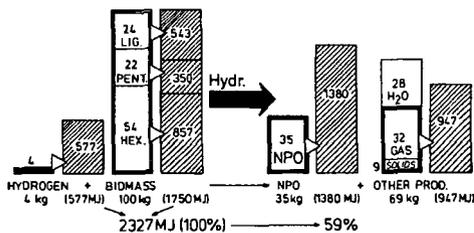


Figure 3 Energy Balance for hydrocracking of biomass

The variation of process parameters was also studied and is documented in various publications (7-9). There is a positive correlation between the pressure and the yield of liquids and a negative correlation between the pressure and the amount of char. At 3 MP initial hydrogen pressure the char yield is as high as 40 % but between 10 and 13 MPa, char formation is very low and amounts to ca. 5 % (8) (see Figure 4). The chemical characterization of the NPO's was mainly done by capillary gas chromatography and mass spectrometry with special emphasis on the qualitative and quantitative determination of phenolics which industry is mostly interested in. However, the unambiguous assignments of reaction products was difficult for the slurry oil phase reactions because the recycling oil was also degraded to a certain extent.

Therefore, we carried out hydropyrolysis experiments without a co-solvent using the same conditions as before in the hydrocracking experiments. Beside spruce wood and china grass, we also included technical lignins from various pulping processes as feedstocks in our experimental designs. Conversion of the feedstocks was excellent (10-12). In some cases, at suitable conditions, no char was formed. In general, lignins gave very high liquid yields of up to 80 %. VEBA OEL, the largest German refinery company, showed interest in lignin

hydrocracking for phenol production as methyl-aryl-ethers can be used as octane enhancers in gasoline. For this reason, we concentrated our work on lignin. A lot of experiments were performed at IWC including the application of slurry oils derived from petroleum and lignin. Despite of the high conversion rates, the amount of mono-phenols did not come up to our expectations. In the best case the yield of monomeric phenols was around 13 wt% (13,14).

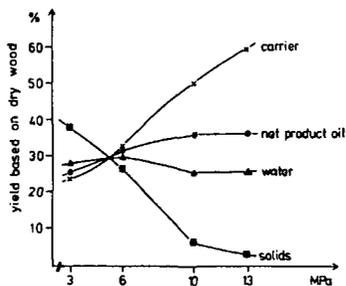


Figure 4 Yield of hydrocracking products at different initial hydrogen pressures

#### FLASH PYROLYSIS OF BIOMASS IN A FLUIDIZED-BED REACTOR

Since the aforementioned workshop on flash pyrolysis, several technologies have been developed mainly in Canada and the United States. At the moment, the most advanced flash pyrolysis technologies available are from ENSYSN, Gloucester, Ontario, Canada, (circulating fluidized bed), the University of Waterloo, Waterloo, Canada, (stationary fluidized bed) and NREL, Golden, Colorado, USA (vortex reactor). The Canadian know-how is now being exported to Europe. Especially the Waterloo Fast Pyrolysis Process (WFPP) is applied in research laboratories in Spain, Great Britain, Finland, and Germany. The first pilot plant of the WFPP process, with a capacity of 200 kg/h, was installed in Spain funded by the EU and UNION FENOSA, a Spanish energy producer. Another pilot plant from ENSYN, Canada, will be erected in Italy in 1995. A typical mass balance of the flash pyrolysis process is shown in Figure 5. The elemental composition of the liquids is very similar to wood. Their quality is quite different from high pressure oils. They contain water (10 to 35 %) and are rich in oxygenated compounds. Pyrolysis liquids are corrosive due to their low pH-value and thermally unstable because they tend to condensate at elevated temperatures. Therefore, the direct use is difficult and upgrading is necessary depending on the application.

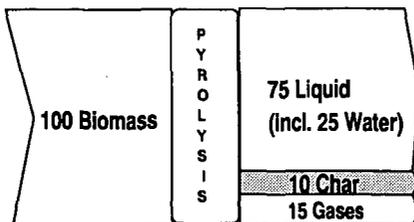


Figure 5 Mass balance of flash pyrolysis

Recently, the investigations on thermochemical conversion at IWC were also extended to flash pyrolysis using a continuously operating bench scale fluidized-bed reactor from the University

of Waterloo with a capacity of 100 g/h. A reactor description is given elsewhere (15). There are several reasons why fast pyrolysis is now so attractive:

1. There is an increased interest in the EU to produce biofuels by flash pyrolysis for the production of power, transportation fuels, and chemicals.
2. ICW is involved in a EU research project on "Integrated Chemicals and Fuels Recovery from Pyrolysis Liquids Generated by Ablative Pyrolysis". Within this project we can use our expertise in analysis, fractionation, and upgrading of bio-oils.
3. IWC got funds from the German Foundation for Environment to investigate the possibilities of using the flash pyrolysis technology for the disposal of contaminated wood waste.

For this purpose a 1 kg/h pilot plant with a fluidized bed reactor and gas recycling will be erected at IWC in 1995. Flash pyrolysis in fluidized beds has some advantages over conventional incineration of waste wood which actually in Germany is very limited due to legislative restrictions. (1) the gas volume in the process is drastically reduced. Thus, gas cleaning is more easier, (2) the formation of dioxins is unlikely to occur due to the absence of oxygen, (3) the plant capacity can be very small.

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Table 1 Main processes and characteristics for the thermal conversion of biomass

Technology	Main characteristic	Catalyst	Temperature (°C)	Pressure (bar)	Residence time	Main primary products, application, comments
Combustion	O <sub>2</sub> /air in excess	N	ca. 1000	N	short	heat
Gasification	O <sub>2</sub> /air limited (also with steam)	Y/N	1000-1500	Y/N	short	synthesis gas, fuel gas, ethene, ethin, ... "I C chemistry" ... "indirect liquefaction"
Pyrolysis	inert gas atmosph.	N	> 450	Y/N	very long (hrs, days)	charcoal (carbonisation)
Pyrolysis	inert gas	N	>450	N	short (> min)	fuel gas, liquid tar (low yield), solid char
Pyrolysis	inert gas	N	>450	N	very short (< sec)	(flash pyrolysis) aqueous, acidic liquid tar for fuel (high O content) and chemicals
Pyrolysis	inert gas	Y	various	reaction conditions	various	catalytic pyrolysis under development
Liquefaction	CO (H <sub>2</sub> ) in H <sub>2</sub> O/alkali	Y	350-400	300	>15min	sometimes in combination with pretreatments, O content of liquids is still high
Hydro-pyrolysis	H <sub>2</sub> atmosph. (gas/solid phase)	Y	350-600	50-200	>15 min	low viscous oil in high yield, low O content
Hydro-cracking	H <sub>2</sub> atmosph. (gas/liquid phase)	Y	350-450	50-200	>15 min	low viscous oil in high yield, low O content
Hydro-treating	H <sub>2</sub> atmosph. (gas phase)	Y	various	reaction conditions	various	used for upgrading of pyrolysis oils, O content below 1 %