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# THERMAL AND THERMO CATALYTIC CO-CRACKING

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# ABSTRACT

The catalytic co-cracking of biomass, polymer waste, or brown coal could be an economical process for production of high value added aromatics components, which are obtained from crude oil currently.

In this study thermal and thermo-catalytic cracking of polystyrene waste was carried out to produce aromatic hydrocarbons. A synergistic effect between the coated metal mesh and the melted polymer was observed, that promoted the production of liquid aromatics fraction significantly.

## **1. INTRODUCTION**

The demand of mankind for raw materials and energy is on the rise due to both a growing population and standard of living. With continuous growth of the use of fossil fuels the degree of waste treatment has a rising tendency. The two processes cannot be separated from each others therefore it is important that a competitive and sustainable global energy need be ensured with a lowest possible harmful environmental emission.

The main research direction for processes based on biomass cracking - today mainly co-cracking - is the utilization for energetics purposes as this way the dependence on fossil fuels can be reduced. However, to allow for the achievement of a process working at the proper efficiency and economy it is important to know that kinetics of thermal decomposition, reaction mechanism and - often - quite significant interaction of heterogeneous components.

Bio oil produced from pure biomass by catalytic thermal cracking - by nature of the raw material - has high oxygen content, due to which storage, corrosion and chiefly stability problems arise. To produce oil of high quality - with high isoparaffin content - further catalytic isomerisation and hydrogenation processes are required, which is detrimental from an economic point of view [1]. It can generally be said that the latest trends of today's research investigate the opportunities of co-pyrolysis meaning co-processing of more than one substance flows. A number of scientific publications report that the quality of oil produced was enhanced this way thereby production costs can de decreased considerably. It begins to be accepted both in Hungary and at an international level that polymer (plastic) waste and/or cole mingled with biomass can not only improve the quality indicators of oil in the final product but also can provide a long-term tool for tackling significant environmental and waste treatment issues.

Raw materials of co-cracking experimentation: polystyrene (waste fraction), biomass, combinations of lignite of various quantities. The admixing of the latter two into material flow depends on the polymer reference measurement, which does not take place in the current phase of experiments.

The aim of research is to carry out comprehensive experiments focussing on interactions arising during thermo-catalytic thermal cracking of plastics and/or cole mixed with biomass raw material, which interactions promote the formation of fluid phase.

# 2. PRESENTATION OF RAW MATERIALS AND EQUIPMENT OF THERMAL AND THERMOCATALYTIC THERMAL CRACKING

## 2.1. Presentation of raw materials applied

The various artificial polymer derivatives (plastics) have become important structural materials of mankind. The use of plastics has risen significantly in the last 100 years, consequently various types of polymers are increasingly prevalent in the resulted waste. Their production needs high quantities of fossil fuels as their main raw material for production is crude oil. Because of this it is important to consider polymers that have become waste to be a secondary source of raw materials as thereby the environmental load of harmful landfills on nature can be reduced and global  $CO_2$  levels can be lower as well.

Using coal is beneficial as it makes up of 65% in fossil fuels, furthermore it shows a more even distribution on Earth than oil and gas reserves since its large quantity is available for over 70 countries [2]. These relevant geological factors suggest a role of importance for the future use of cole. According to literature data the decisive ratio (78%) of energy consumption of the world is constituted by fossil fuels (oil, natural gas, coal) [3]. By revealing the mechanisms the operational parameters of chemical industry processes for co-cracking can be further enhanced leading to the more economic production of more value-added products.

## 2.2. Presentation of experimental equipment

Figure 1 shows the circuit diagram of the equipment used for the measurement. The raw material is infed in the vertical reactor '3' in steps of batch. The reactor tube is heated with Hőker Cső 250/900 electrically heated furnace whose nominal power is 650 W. The furnaces are shown in Figure 2. In the experiments the vertical reactor operated at 450°C.

The structural material of tube reactors were 1.4845 (H9) grade austenitic heat resisting steel. The temperature was controlled by a proportional–integral–derivative (PID) controller.



Figure 1 The workflow of the constructed equipment. 1. nitrogen bottle; 2. furnace\_01; 3. vertical reactor; 4. horizontal reactor (catalyst attachment); 5. furnace\_02; 6. condenser; 7. fluid collector; 8. rotameter

It is important to mention that there is no significant difference between the mechanisms of conventional cracking and that of co-pyrolysis/cracking. The process is performed in oxygen-free atmosphere, closed reactor system and at a moderated temperature in both cases. Depolymerization reactions are endotherm processes therefore the power used for heating must be provided from an external source [4].



Figure 2 Photographs of the laboratory equipment depicting tube reactors '3' and '4' and the furnaces.

#### 2.2.1. Preparation of raw material

Before starting the experiment we crushed raw materials to a particle diameter of 2 to 3 mm in order to ensure an optimum heat distribution. Next, a half an hour long drying took place at 105°C in the vertical reactor '3'. It is important to remove humidity (corrosion, product contamination) at a highest possible efficiency for further operations as well [5].

#### 2.2.2. Process of cracking

The drying process finished, cracking was carried out. After the infeed of raw materials, the process was initiated by incorporating an inert gas  $(N_2)$ . Through the incorporation of nitrogen the reactor system was freed from oxygen and we also checked appropriate gas tightness.

The incorporation of inert gas is optional, it is mostly an economic decision as the operation of compressor and gas are costly. However, by means of this the residence times of volatile products in the heated zone can be controlled (in an optimal case less than 2 s), thus, secondary cracking can be minimized and thereby the quantity of oil fraction can be increased [6]. In case of fluid bed and circulation fluid bed reactors the flow rate of inert gas has an optimum as an overly high rate can have a negative effect on the product quantity as well [7].

For safety reasons at this point we only tested the incorporation of nitrogen during measurements. Its effect on the product distribution has not been investigated but we would like to optimize the mentioned parameter too, as reactor systems arranged in different positions create specific flow circumstances.

After reactor '3' product steams proceeded to the horizontal reactor system '4' (Hőker Cső) where they passed the catalyst attachment whose temperature was kept at 300°C during the experiments. Various catalysts and purely thermal cases show different results.

#### 2.2.3. Product separation

The hydrocarbon steams of temperature of 300°C leaving the horizontally-arranged reactor are condensed in the heat exchanger '6' to 20°C. The condensed fractions are gathered in the fluid collector while C1-C5 gases were flared during experiments.

The quantity of gas, fluid and solid hydrocarbon fractions varied significantly during the experiments in function of thermal and thermo-catalytical cases. The weight of forming fluid or solid remains can be measured extremely precisely, which allows the determination of quantity of gas yield in each case. The following section covers the results of the measurements.

#### **3. PRESENTATION OF RESULTS AND METHOD**

## 3.1. Presentation of measurement method

We performed 3 measurements each on the constructed equipment. In the first 3 steps cracking was carried out thermo-catalytically using a homogeneous polystyrene raw material. In the vertically arranged reactor body a coated metal net was applied between the drain valve and polystyrene. In the catalyst attachment (horizontally arranged reactor body) a zeolite catalyst was placed, in which only hydrocarbon formed in the process were in contact.

In the second phase of experiments (3 parallel measurements) a coating-free metal net was applied and no catalyst was used in the catalyst attachment, the temperature of the reaction space being held at only 300°C.

The experiments were performed for 50 minutes in each case as no fluid product came into being after 40 minutes. Heating was stopped after 50 minutes. The heating of reactors was realized with the temperature profile shown in Figure 3 (Time-temperature relations of catalytic measurement 1).



Figure 3 Time-temperature diagram of catalytic measurement 1 (300°C: catalyst attachment, 450°C: reactor)

Figure 3 shows that heating rate of furnaces were set to a value of 14 to 20°C/min. The interval of 22 to 28 minutes reveal that the temperature exceeds the targeted 300 and 450°C. This phenomenon is due to the fact that the 'D' parameter of PID controller of furnaces cannot set the controlled characteristic to the base parameter therefore it overshoots. The effect can cause an error whose degree raises further open questions.

#### 3.1. Presentation of material balances

Figure 4 shows the results obtained by means of experiments carried out on the experimental equipment. Three groups can be distinguished in the figure: gas, fluid and solid state hydrocarbon products. The results of the thermo-catalytic measurements are indicated in the first 3 columns as blocks.

It is seen that using a catalyst and coated metal net results in: the formation of 8.1 g gas, 23 g fluid, as well as 8.8 g solid state hydrocarbon product.



■ 1. Catalytic case ■ 2. Catalytic case ■ 3. Catalytic case ■ 1. Thermal case ■ 2. Thermal case ■ 3. Thermal case

#### Figure 4

# Gas, fluid and solid state hydrocarbon fractions measured in catalytic and thermal cases indicated in weight%.

The second 3, purely thermal measurements are indicated in columns 4, 5 and 6 as blocks in Figure 4. On average: 23.8 g gas, 1.7 g fluid, as well as 14.5 g solid state hydrocarbon product were formed.

Figure 5 shows the fluid state mixture produced in the thermo-catalytic measurement 2.



## Figure 5

Fluid state hydrocarbon product produced in the thermo-catalytic measurement 2

As in thermal cases the formed oil-like fraction was insufficient for qualitative analysis, therefore at this time only the quantitative analysis of fluid samples produced in catalytic processed was executed. The experiment was conducted according to MSZ 1448-4:1198 standard on volatile aromatic hydrocarbons whose results are listed in Table 1.

G	Measurement	Measurement	Measurement
Component	1		3
	mg/I	mg/I	mg/I
Benzene	974	961	1 010
Toluene	45 000	46 200	47 300
Ethyl benzene	30 900	30 920	29 033
m+p xylene	20 100	19 300	21 100
o xylene	293 000	291 000	296 000
In total	389 974	388 381	394 443

Table 6The composition of fluid products produced thermo-catalytically

The fluid fraction with nearly 390g/l aromatic contents listed in Table 6 can be considered a very good result from the point of view of industrial use.

Figure 7 shows the solid state strongly unconverted polystyrene raw material formed during thermal measurement 1.



Figure 7 Solid state strongly unconverted polystyrene raw material formed during thermal measurement 1.

# 4. CONCLUSIONS AND DETERMINATION OF RESEARCH GOALS

It appears from the measurement results that the quantities of hydrocarbon fractions obtained during thermal and thermo-catalytic measurements presented significant differences, which influence was most visible for fluid products. The tenfold fluid yield, which accompanies thermo-catalytic cases, was not expected, therefore it is presumable that it was due not only purely catalytic effects. The application of a catalyst promotes reactions happening at a higher conversion, which can increase fluid and gas yields (to a maximum double value according to earlier experience) compared to purely thermal cases. Therefore the clarification of the exact causes requires further experiments.

The paramount goal of our research work was to enhance the quantitative and qualitative indicators of producible fluid in every respect.

The background of high differences may not only hide the catalytic processes of catalyst attachment as the vertically arranged reactor produced just as the double quantity of solid remain in a thermal case. Thus, two things are presumed basically:

- 1. the coated metal net has a catalytic effect on the decomposition process,
- 2. touching the heated wall, the metal net resulted in a better and more intense temperature distribution in the polymer melt, therefore it cracked at a higher degree. Therefore the quantity of solid remnants could decrease while the quantity of fluid and gas products increased.

The goal of future research is to set up and implement a comprehensive measurement plan, which is suitable to determine to what extent the catalytic as well as thermal conduction ability of coated metal net increase fluid and gas yields. The revelation of exact causes can contribute to the optimal design of industrial reactors used for cracking.

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