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ANALYSIS OF A THERMO-CATALYTIC CRACKING

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Abstract: The core topic of the current research is composed of chemical raw materials to be produced from renewable and waste sources, out of which the most significant future representative can be the so-called thermo-catalytic cracking process in combined material flow. The thermo-chemical conversion of biomass and/or plastic waste(s) is a process, by means of which base materials for the chemical industry or energy carriers can be manufactured. If one considers the conventional, purely thermal not catalytic cracking of biomass only, the quality indicators of the so-called bio oil to be produced such as heating value, viscosity, oxygen content etc. are fairly poor. Today's research investigates thermo-catalytic cracking performed in combined material flow (biomass and synthetic polymer waste) gaining popularity, by means of which one can efficiently attain quality improvement during the process from the aspect of liquid products to be produced. The liquid product obtained from thermo-catalytic thermal cracking of pure biomass was a brownish-black pitchy fraction. By adding 50 wt% PS (polystyrene) waste, a considerable qualitative and quantitative improvement could be achieved during the combined thermo-catalytic cracking. The aromatic hydrocarbon content of the liquid product increased considerably. In addition, the quantity of solid chark and carbonised fraction remaining in the reactor body dropped by 36% on average in favour of the liquid and gas products, which may significantly promote the technical-economic viability of the technology.

Keywords: cracking, biomass, recycling of plastic waste, aromatic hydrocarbons

INTRODUCTION

The line of main direction of research is the optimisation of conversion possibilities of lignocellulose-based biomass into a valuable chemical raw material. Tests were performed using maize stalk and manmade difficult-to-recycle synthetic polymer waste. The use of the developed experimental process can be a considerable alternative application and/or recycling option for both components against deposit of waste or controlled/uncontrolled incineration. The purpose is to optimise operational parameters of the thermo-catalytic thermal cracking chemical process in combined material flow, which is based on the enrichment of aromatic hydrocarbon content in the produced liquid products. Aromatic hydrocarbons are unsaturated ring carbon compounds that can all be derived from benzene of the empirical formula C_6H_6 in terms of their structure. Benzene, toluene and ethyl benzene are main base materials for the important and a large number of intermediates that are used to manufacture synthetic fibres (polyester, nylon, etc.), resins, artificial rubbers, explosives, pesticides, detergents, paints and many base materials indispensable for the industry. Approximately 35 million tons are manufactured from these compounds globally. The main decision factors in the selection of raw materials for manufacture are their availability and chemical composition. Currently the largest quantities of benzene, toluene and xylene are produced from crude oil or coal [1].

Due to the depletion of fossil energy carriers and the increasing demand for the aromatic hydrocarbons, research gains importance in future for possible alternative base material sources.

CHARACTERISTICS OF THE RAW MATERIALS

As a renewable energy source to be used, biomass has an increasing significance since it contributes to global CO_2 emission levels to a much lower extent – via the closed carbon cycle. One of the raw material for the research was maze stalk, which is an agricultural by-product generated at the highest quantities in Hungary [2]. The cellulose-containing biomass, jointly called lignocelluloses contain cellulose, hemicellulose as well as lignin in different quantities depending on the type and advanced state of the plant in question, which natural polymers make up 85 to 90% of dry matter [3]. A general fact is that biomass can be converted directly into gas and liquid products as well via biomass thermal cracking.

However, because of the structure of its raw material, the liquid fraction obtained from cracking pure biomass has a high oxygen content [4-5], therefore its usability is restrained strongly. Nowadays it is an area of intensified research, the quality of target fractions by combined degradations of plastic wastes rich in hydrogen to what extent exactly and under which operational as well as raw material combinations can be improved or carried out.

Artificial polymer derivatives have become the most important structural materials of mankind. The use of plastics has risen significantly in the last 100 years and the various types of polymers are increasingly prevalent in the resulted waste. The various plastic materials are produced globally in large quantities and their manufacturing capacity rises by an average 10% yearly since the 1950s [6].

Due to the mentioned relevant causes, the other raw material in the subject matter of examinations is polystyrene whose annual production capacity reaches 16 million tons globally and the plastic type in the most widespread use in Hungary. Once it loses its utilisation function, however, its is harmful to environment, being a not readily biodegradable waste, whose treatment is a relevant environmental issue, moreover, a real logistic challenge in the case of foamed PS (polystyrene) at the same time. The real trouble is that the majority of PS is not used as a durable product, thus, it appears in a high proportion in municipal waste such as a disposable dish, glass, cutlery etc. contaminated with foodstuff, whose recycling is still at an embryonic stage [7]. The structure of polystyrene is depicted in Figure 1.

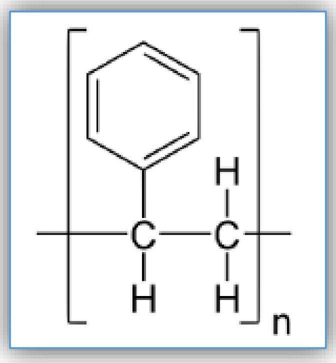

Figure 1. Structure of polystyrene

Figure 1 reveals that PS is purely composed of hydrocarbon, which is particularly beneficial for cracking processes because the releasing hydrocarbon saturates the unsaturated carbon-chains, which can lead to a qualitative improvement.

CHALLENGES OF TECHNOLOGY

The future viability for processes processing biomass and plastic waste in a combined way has many crucial points. Because of the uncertain composition of waste and biomasses, the input material flow is uncertain, which is a large deviation to the general chemical processes. On top of that, it is also particularly important in the design that special properties of raw materials in question must be taken into account such as the polymer structural properties, low heat conductivity and visco-elastic behaviour [7].

Furthermore, it should be highlighted that it is indispensable to know the kinetics of thermal decomposition, reaction mechanism and quite significant interaction of heterogeneous components for the design of the process working at the proper efficiency and economy.

All in all, it can be said that thermo-catalytic cracking in combined material flow can be one of the future's significant viable alternative to manufacturing base materials for the chemical industry. At present, the improvement in the qualitative indicators of hydrocarbons produced so are faced with major difficulties and keeps raising many unanswered questions.

PROCESS CHARACTERISTICS

The fundamental difference between thermal and thermo-catalytic thermal cracking (cracking, pyrolysis) resides in the fact that no catalyst is used in the former. A joint feature is that polymers with long carbon-chains degrade during the process into smaller molecules, which means actually the basis of recycling. Another essential feature of the technology is that the process takes place in an inert atmosphere (oxygen-free), at near atmospheric pressure. The great advantage of thermo-catalytic cracking over purely thermal cracking is the following:

- Smaller reaction temperature, which results in lower energy consumption;
- Cracking reactions occur faster allowing for shorter residence time and lower reactor volume;
- The yield of various more valuable components can be optimised by selecting an appropriate catalyst;
- The ring, branched and aromatic hydrocarbon contents in the product fraction increase by thermo-catalytic cracking of polyolefins, which raises the economic potential of the process [8].

Thanks to its many positive literature and industrial references, the well-known and widely used catalyst ZSM-5 was employed in our examinations.

EXPERIMENTAL EQUIPMENT

The implemented laboratory-scale thermo-catalytic equipment is illustrated in Figures 2 and 3 from side and top views.

Figure 2. Experimental equipment showing a side view

Figure 3. Experimental equipment showing a side view

The workflow of the experimental equipment is detailed in Figure 4.

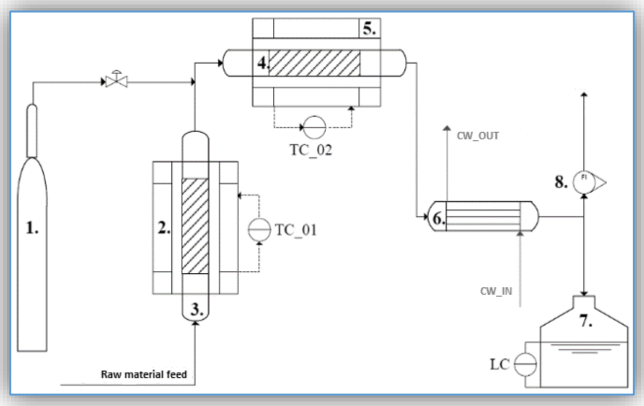

Figure 4. The workflow of the experimental equipment: 1. nitrogen bottle, 2. furnace, 3. vertical reactor, 4. horizontal reactor (catalyst attachment), 5. furnace, 6. condenser, 7. fluid collector, 8. rotameter

The raw material was fed in the vertical reactor '3' in steps of batch. The reactor tube was heated with a 'Hőker Cső' 250/900 electrically heated furnace whose nominal power was 650 W. The furnaces are shown in Figures 2 and 3. The structural material of tube reactors were 1.4845 (H9) grade austenitic heat resisting steel. The temperature was controlled by a PID.

STEPS OF MEASUREMENTS

An individually designed tube reactor system was used for the measurements.

250 gr of solid materials was cracked off in the series of experiments. On five occasions, purely biomass and on five occasions 50-50 wt% PS and maze stalk, in each case using 12.5 gr of the catalyst ZSM-5.

The experiments ran for 50 minutes. The raw material was infed in a batch operation in the vertically positioned tube reactor. The reactor atmosphere was inertised by means of nitrogen in the first step. In the second step the temperature of the reactor was adjusted. Product yields were examined versus time at 450 °C.

During the experiments, the hydrocarbon steams left the vertically-positioned reactor body to the horizontal tube reactor. Product steams left from this into the condenser where they were cooled down to 20 °C. Afterwards, the liquid phase was gathered in the liquid collector and the gas phase was flared off.

RESULTS

In cracking the maze stalk (250 gr.) on average: 111 gr. solid, 40 gr. liquid and 99 gr. gas product were generated, which corresponded 44.4, 16 and 39.6 wt%, respectively, related to the quantity of the input raw material.

In cracking the maze stalk and polystyrene in 50-50% in combined material flow on average: 21 gr. solid, 124 gr. liquid and 105 gr. gas product were generated, which corresponded 8.4, 49.6 and 42 wt%, respectively, related to the quantity of the input raw material mixture. The results are illustrated in Figure 5.

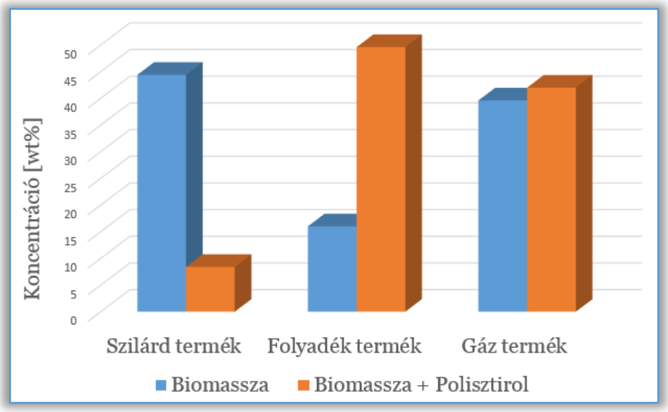

Figure 5. Results by cracking of biomass and biomass + PS waste by wt%

The results shown in Figure 5 reveal clearly that the PS waste added to biomass greatly enhances the yield of valuable liquid product, while the quantity of chark and carbonised phases harmful to the process from several aspects dropped to a large extent.

The produced liquid products were analysed qualitatively as well. The tests were carried out according to MSZ (Hungarian standard) 1448-4:1198 volatile aromatic hydrocarbons. The results are summarised in Table 1.

Table 1. Concentrations of aromatic components [mg/l].

Component	Biomass [mg/l]	Biomass and polystyrene [mg/l]
benzene	12	954
toluene	345	45322
ethyl benzene	234	30444
m+p xylene	154	19876
o xylene	432	280021
In total	1177	376617

Table 1 shows that the quantities of aromatic hydrocarbons reach the value of 376 gr/l on average in cracking in combined material flow, which indicates a serious qualitative improvement in relation to the purely biomass raw material.

CONCLUSIONS

The results absolutely support the advantage of process in combined material flow over the cracking purely maze stack as the quantity of valuable liquid product jumped significantly, by 33.6 wt% on average. The quantity of carbonised phase and char fraction harmful to the process dropped (on average by 36%). These results are due to the fact that a considerable quantity of hydrogen was released from the thermo-catalytic degradation of PS, which saturates the carbon-chains of the hydrocarbon steams forming from the biomass during the process, in the presence of the catalyst ZSM-5. There was no significant difference for the gas products.

Due to its structure, PS can produce a significant amount of aromatic hydrocarbon of liquid state 450°C, which was demonstrated clearly during the measurements as a concentration of 376 gr/l was gathered on average.

It is visible based on the measurement results that more valuable and larger quantities of chemical raw material can be produced by thermo-catalytic cracking in combined material flow of maze stalk and PS waste, which can shift in the focus of attention increasingly in future because of diminishing crude oil reserves.

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