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PYROLYSIS TECHNOLOGIES FOR BIOMASS AND WASTE TREATMENT TO FUELS AND CHEMICAL PRODUCTION

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Abstract

The second generation of biofuels processes should differ from the first in a) utilizing the whole plant as a feedstock and b) use of "non-food" perennial crops (woody biomass and tall grasses) and lignocellulosic residues and wastes. Possible options for the conversion of these lignocellulosic plant materials include: thermal cracking, catalytic cracking, pyrolysis, carbonisation, catalytic reforming, steam reforming, gasification, Fischer-Tropsch synthesis, hydro-dehydrogenisation, hydrocracking, hydrorefining and decarboxylation. The main goal of biorefinery is to produce high-value low-volume chemicals (levoglucosan) and low-value high-volume fuels with a series of unit operations.
Thermal processes must be included among the attractive basic recycling technology for polymers for which thermal cracking and pyrolysis enable the conversion of polymer materials into fuels, monomers and other valuable products. The subject of the research were the thermal and catalytic processes for the production of motor fuels from polymer material from industrial material or municipal trash sources turning it into sulfur free, non-aromatic and ecological fuel via chemical recycling to replace fossil fuels mainly from oil sources. The key is the liquefaction of polymer materials to oil/waxes that can be distilled to provide gasoline, diesel fuels and heating oils that can be used directly or after hydrorefining.
We found a way, how incorporate polymer waste into conventional liquid steam cracking feedstocks. Polyalkene oils and waxes decompose during co-pyrolysis. Amount of desired alkenes (ethylene, propene) increases or is slightly less in dependence on polymer type. Mixture of waxes in heavy naphtha (10-20% mass) exhibits short tendency to coking. Feedstock and chemical recycling of polyalkenes oils and waxes via co-pyrolysis is a very promising method treatment of polymer waste.
We have developed Deep Scavanger Steam Cracking process or Steam Cracking Activation process (DSSC/SCA) for thermal cracking of used tyres and rubber waste, that works in a flow reactor. Basically, we received three fractions from the thermal cracking of used tyres-gases, liquid oils (d, l- limonene) and solid residues (coke, carbon, steel).

Key words: pyrolysis; petrochemistry; carbonization; biofuels; carbon; levoglucosan; d,l – limonene; DSSC/SCA; wastes.

1. Petrochemistry

Pyrolysis is endothermic cracking process requires large energy supply at higher temperature with short residence time of the cracked products. The equilibrium resulting in formation of elements C and H_2 must be preveated by short residence time (quenching). The discovery that alkenes can be produced in high yields from both alkanes present in natural gas and from petroleum fractions has laid the foundation for what is now known as the petrochemical industry. The principal process used to convert the relatively unreactive alkanes into more reactive alkenes is thermal cracking, often referred to as „steam cracking". This process produces mainly ethene, but valuable co products such as propene, butadiene, and pyrolysis gasoline, with benzene as a major constituent, are also produced.

Since the late 1930s, when the petrochemical industry stared to take shape, ethene has almost completely replaced coal-derived acetylene and now is the largest volume

building block for the petrochemical industry. Its main outlet is the production of polyethylenes (> 50%), followed by vinyl chloride, ethene oxide and styrene.

In steam cracking a hydrocarbon stream is thermally cracking in the presence of steam, yielding a complex product mixture. The name steam cracking is slightly illogical : under the reaction conditions steam is not cracked it functions primarily as a diluent, allowing higher conversion. A more accurate description of the process might be „pyrolysis", which stems from Greek and means bond breaking by heat. The main product of steam cracking is ethene, which is a very important base chemical. World ethylene capacity increases 2 million tpy in 2007. Capacity as of Jan. 1, 2008, was 119,6 million tpy, an increase from 117,6 tpy of capacity reported in last year's survey [1]. Olefin production capacity has virtually doubled in the past 15 years. Current capacity is approximately 130 MM tpy and demand is about 114 MM tpy [2]. Present olefin-plant capacities, investment costs, equipment delivery schedules and construction timetables represent many of the industry's major challenges. These concerns were true in the late 1990s when largest cracking furnaces (ethane and naphtha types) were constructed, and when the largest total plant capacities approached 1,500.000 tpy (1,5 MM tpy). As current projects, prices and participants have extended plant size and upstream/downstream links, these challenges must be addressed in conjunction with key equipment manufactures. Ongoing design of key equipment corresponds to respective nominal naphtha/ethane cracking capacities of 1,5 MM tpy to 2 MM tpy for future ethylene plant designs.

The industry has responded well to the increasing plant capacity demands and improved operational efficiency. Accordingly, equipment disposition and item count within today's olefin units is actually less than it was a generation before. New plant designs have increased specific capacities of key items significantly. Newer olefin facilities have integrated several heat and mass transfer facilities, combined various equipment vessels, expanded catalytic reactor capacities, extended heat pump links between standard compressors and fractionators and significantly in creased key equipment duties/capacities.

Early smaller ethylene plants often contained up to 20 individual cracking furnaces. For example a major European unit, constructed 35 years ago, had an initial processing capacity of 450 M tpy and used 16 fresh-feed furnaces plus two recycle furnaces. Today, the standard liquid-feed furnace sizes are seven times larger. Gas–feed cracking furnaces produce even higher ethylene yield outputs.

The latest designs for liquids-cracking furnaces use symmetrical U-type radiant coils; furnace capacities have increased by up to 25% within identical radiant firebox dimensions. One of the largest naphtha-cracking furnaces currently under construction will produce 190 Mtpy ethylene [2].

2. Carbonization of coal

Coal was important to the chemical industry in the nineteenth and early twentieth centuries. It provided calcium carbide and hence acetylene, synthesis gas and hence ammonia and methanol, petroleum-like fuels, and all the aromatic chemicals contained in coke oven distillate. When coal is heated in the absence of air to a temperature of about 1000°C (pyrolysis; high-temperature carbonization of coal), coke forms together with many liquid and gaseous products. It is this distillate, also called coal tar, that provided the aromatics and many other chemicals for the early chemical industry. The coke is almost pure carbon and is used in steel manufacture which, as it becomes more efficient and process change, requires less coke. Nonetheless some coke will always be needed, and therefore the chemical industry will always have available the chemicals that volatilize from the coke ovens. A typical coking operation produces 80% coke by weight, 12% coke oven gas, 3% tar, and 1% light oil consisting of crude benzene, toluene, and xylenes [3].

3. Manufacturing of activated carbon

Activated carbon is the collective name for a group of porous carbons, manufactured by the treatment of a char with gases or by carbonisation of carbonaceous materials with simultaneous activation by chemical activation. All these carbons are prepared to exhibit a high degree of porosity and an extended internal surface area.

Almost any carbonaceous material may be used as precursor for the preparation of activated carbon. However, in practice, wood, nut shells and fruit stones, peat, charcoal, brown coal, lignite, bituminous coal, petroleum coke, etc. are inexpensive materials with a high carbon content and low in inorganic components and consequently are adequate for the production of activated carbon although the properties of the final products will

differ depending on the nature of the raw material used, the nature of the activating agent used and the conditions of the activation process.

The preferred raw materials for the manufactures are lignocellulosic materials account for 47 wt. % of the total raw material used for the actual preparation of activated carbon but there are significant differences between the various types that can be used. Low density materials like wood, which also contain high volatile content, produce activated carbons with large pore volume but low bulk density but if the process is modified to decrease the loss of carbon during carbonization, or the carbon is densified, the quality can be considerably increased [4]. On the other hand, coconut shells, fruit stones (pits), and similar materials, which have high bulk density and volatile content, produce hard, granular carbons with large pore volume and are suitable for many applications. The wood account for 130 000 tonnes per year is used for the actual preparation of activated carbon.

There are two principal methods of manufacturing activated carbon, physical and chemical activation. The former implies the carbonization of the raw material in an inert atmosphere followed by partial gasification of the resulting char with steam, carbon dioxide, or a mixture of them. In chemical activation the raw is impregnated with a chemical such as phosphoric acid or zinc chloride and the impregnated product is pyrolyzed and then washed to remove the activating agent.

The furnaces used for the production of activated carbon can be of different types: rotary kiln, multiple hearth, vertical shaft and fluidized-bed. Most companies use internally heated rotary kilns, since they are suitable for production of activated carbon of a large range of particle sizes. These are furnaces of large dimensions. The residence time of the carbon in rotary kilns is usually much larger than in other types of furnaces. Multiple hearth furnaces, with rotary arms and stationary floors on each stage have the advantage over rotary kilns of a better control of temperature (400 – 900°C). Residence time in this type of furnace is much shorter than in rotary kilns.

Pyrolytic carbons, e.g. deposited slowly from methane in helium is a well-ordered form of carbon, approaching the quality of single crystal graphite. It was developed together with nuclear grade graphites as a cladding material for spherical fuel elements. Its applications then waned until the advent of the carbon fibber/carbon composite when it became one matrices of carbon materials within the weaves of the carbon fibbers systems. It is finding significant application in the carbon composites of modern aircraft disc brakes [4].

The ever optimistic carbon scientist has his attention firmly attached to two new areas of development, i. e. diamond and diamond-like film and the graphitic film, and the fullerenes and nanotubes and rods. The case for the fullerene and nanotube is still being developed. Efforts to make the fullerenes into viable commercial materials are strenuous. The fullerenes came to us from outer space and this generated many new possibilities.

4. Chemicals and fuels from biomass

Pyrolysis can by defined as the direct thermal decomposition of matter in the absence of oxygen. When applied to biomass, an array [5] of useful products can be produced, liquid and solid derivatives and fuel gases. Already in the 1950s more than 200 chemical compounds had been identified from the pyrolysis of wood. Before the onset of the petrochemical era in the beginning of the 20th century, pyrolysis processes were utilized for the commercial production of a wide range of fuels, solvents, chemicals, and other products from biomass feedstocks. Recently, the global problems that are associated with the intensive use of fossil fuels (global warming, depletion of natural resources, security of supply of energy and materials) have led to a renewed interest in (modern varieties of) these processes. The fact that different biomass constituents react differently at different temperatures to yield different spectra of products can be exploited to extract value-added chemicals from biomass as a renewable route products that can be regarded as petrochemical substitution. The concept of staged degasification is a low-temperature thermochemical conversion route to generate value-added chemicals from lignocellulosic biomass. Fig. 1 presents schematic overview of the staged degasification concept and its place in a thermochemical biorefinery.

The main biomass constituents hemicellulose, cellulose and lignin can be selectively devolatilised into value-added chemicals. This thermal breakdown is guided by the order of thermochemical stability of the biomass constituents that ranges from hemicellulose (fast degassing/decomposition from 200 to 300°C) as the least stable polymer to the more stable cellulose (fast degassing/decomposition from 300 to 400°C). Lignin exhibits an intermediate thermal degradation behaviour (gradual degassing/decomposition from

250 to 500°C). Results obtained for beech wood in principle acknowledge the view that the chemical wood components are decomposed in the order of hemicellulose-cellulose-lignin, with a restricted decomposition of the lignin at relatively low temperatures. In the further course of heating, a recondensation of the lignin takes place, whereby thermally largely stable macromolecules develop. Whereas both hemicellulose and cellulose exhibit a relatively high devolatilisation rate over a relatively narrow temperature range, thermal degradation of lignin is a slow-rate process that commences at a lower temperature when compared to cellulose.

Since the thermal stabilities of the main biomass constituents partially overlap and the thermal treatment is not specific, a careful selection of temperatures, heating rates and gas and solid residence times is required to make a discrete degasification possible when applying a step-wise increase in temperature. To enhance the selectivity towards wanted products, catalysts can be applied as impregnants of the biomass, or as an external aid, e.g.. in the form of the fluidisation material in a fluidized bed reactor or in the form of catalytically active fluidisation gas (steam, hydrogen, oxygen, CO_2). Downstream treatment of the primary product vapours in a fixed bed of catalyst is another possibility.

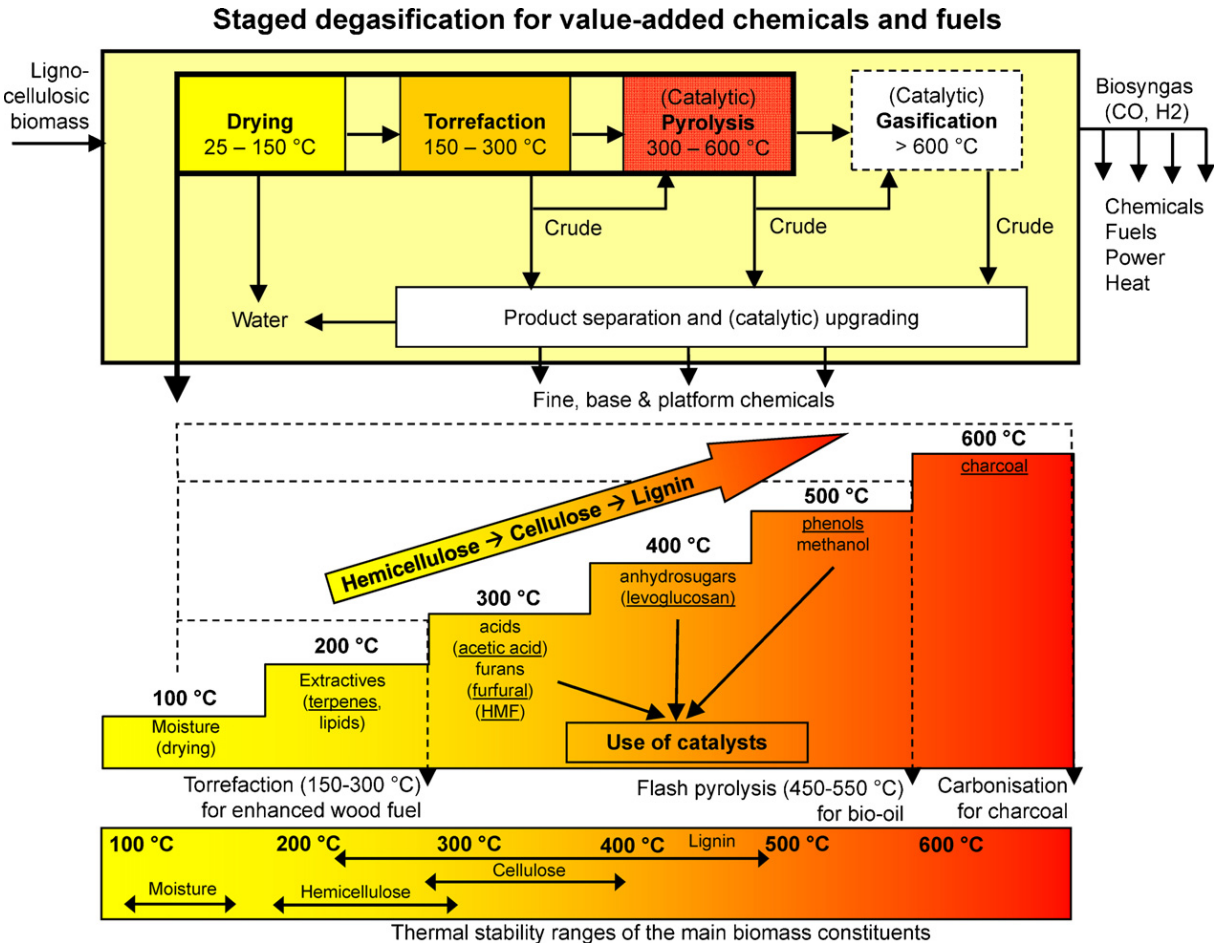

Fig. 1. Staged degasification concept within the thermochemical biorefinery [5](with permission Elsevier, Ltd.)

Depending an these process conditions and parameters like biomass composition, and the presence of catalytically active materials, the product mixture is expected to contain more or less degradation fragments from hemicellulose, cellulose or lignin. The staged degasification approach stands in contrast with fast pyrolysis technology, in which the biomass is rapidly heated up to temperatures around 500°C, causing an almost instantaneous release of a myriad of thermal degradation products that are quickly quenched to a so-called pyrolysis-oil. It is obvious that the extraction of value-added chemicals from this complex mixture of thermal degradation products is a challenge. In their critical review on pyrolysis-oil, Mohan et al. in [5] present an extensive overview of pyrolysis-oil and related issues. Whereas fast pyrolysis of biomass primarily has been developed to maximize liquid product yield, staged degasification aimes at the gentle devolatilisation of thermal degradation products from the biomass. Hereby it is assumed that type, yield and selectivity of the

liberated products can be influenced by matching the process conditions of the degasification process with the thermal stability of the main biomass constituents. Due to the relatively mild conditions, the overall product spectrum might be less complex, more stable and less prone to unwanted secondary reactions when compared to the harsher pyrolysis process where all three biomass components are degraded simultaneously and at the same temperature. Recently, a limited number of value-added chemicals from biomass has been identified in an extensive study by NREL/PNNL. For the carbohydrate fraction of the biomass (hemicellulose and cellulose) furfural and levoglucosan are interesting value-added chemicals that can possibly be produced by direct thermochemical conversion.

Although several (dry) thermochemical processes for furfural production have been explored in the last decades, modern commercial processes to produce furfural involve mostly aqueous phase hydrolysis/dehydration processes operating at relatively low temperatures (around 200°C) and often using catalysts like sulphuric acid. This leaves the anhydrosugar levoglucosan (dehydrated glucose) as the most interesting candidate that could be directly produced from the carbohydrate fraction of biomass by (staged) degasification or pyrolysis. Alternatively, staged degasification could be targeted at the production of groups of chemicals that can be upgraded using existing (petro) chemical technology like selective hydrogenation. Examples of these groups are carboxylic acids (formic, acetic, propionic), furans (furfural, furfuryl alcohol, furanone, hydroxymetylfurfural), C_2, C_3 and C_4 oxygenates (hydroxyacetaldehyde glyoxal, acetol), anhydrosugars (predominantly levoglucosan) and hydroxylated aromatics and aromatic aldehydes which constitute potential thermochemical degradation products from lignin. It is obvious that the separation and subsequent upgrading of these groups of chemicals is easier and cheaper than the isolation of a single chemical from the complex mixture of thermal degradation products.

Product gas samples were analysed off-line with standard gas chromatography-flame ionization and mass spectrometric detection (GC/FID/MS) for most organic, ion-chromatography (IC) for formic acid and Karl-Fisher for water. This standardised method has been developed for the following set of species that are representative for typical thermal degradation products from lignocellulosic biomass : methanol, carboxylic acids (acetic acid, formic acid), other C_2-C_4 oxygenates (acetaldehyde,methylformate, methylacetate, propanal, acetone, 2-butenal, hydroxy-acetone (acetol), 1-hydroxy-2-butanone), furans (alpha-angelica lactone, 5-methyl-2(3H)-furanone, furfural, 5-methyl-2-furaldehyde, furfuryl alcohol, 2(5H)-furanone, hydroxymethylfurfural), levoglucosal, phenols (2-methoxyphenol (guaiacol), 4-methylguaiacol, phenol, eugenol, 3-ethylphenol, 2,6-dimethoxyphenol, iso-eugenol, pyrocatechol, syringaldehyde, hydroquinone), other aromatics (3,4,5-trimethoxytoluene, 1,2,4-trimethoxybenzene). Typically, 40-60% of the total gas chromatographic peak area is attributed to unidenfied components.

The paper [5] describes experimental proof of principle activities for staged degasification, a simple and elegant thermochemical conversion option to valorize lignocellulosic biomass. Due to the overlapping thermal stabilities of the main biomass constituents, degasification of the feedstock during a discontinuous step-wise temperature ramp in an auger reactor (a single screw moving-bed type of reactor), leads to complex mixtures of degradation products, with each staged degasification mixture consisting of small amounts of degradation products that originate from all three main biomass constituents. Except for acetic acid, yields of individual chemicals are generally below 1 wt% (based on the dry feedstock weight). However, certain groups of thermal degradation products like C_2-C_4 oxygenates and phenols are formed in higher yields up to 3 wt%. These results are roughly similar for the four selected biomass types beech, poplar, spruce and wheat straw. The only major difference is the higher yield of methanol and phenols for the deciduous beech and poplar woods when compared to the spruce and the straw. Slow pyrolysis of beech in a bubbling fluidized bed typically yields more water, less permanent gases and char, less methanol and phenols and more levoglucosan when compared to conventional pyrolysis in the screw reactor. The main reasons for these differences are the longer solid residence time and the large gradients in the screw reactor when compared to the fluidized bed. Depending on the added value of the product, a limited yield is not necessarily a drawback for a cost-effective process, provided that product selectivity is sufficient for effective separation and upgrading. Concluding, staged degasification is an elegant thermochemical conversion option to valorize lignocellulosic biomass but to increase product yields and/or selectivity, more R&D efforts are needed, especially towards optimization of reactor conditions, application of catalysts and/or specific biomass pre-

treatment. Indeed, results of a hybrid degasification approach, involving a specific hydrothermal pre-treatment and subsequent solid state ^{13}C NMR characterisation of the solid products, have indicated that significantly higher yields of value-added condensable can be achieved.

Levoglucosan (1,6-anhydro-ß-D-glucopyranose) is a potential chemical obtained from pyrolysis of cellulosic biomass [6]. The utilization in synthesis of various chemicals (especially chiral chemicals) and materials is very promising. Its unique chemical nature , i.e. 1,6-acetal ring and $^{1}C_{4}$ conformation makes it an attractive chiral raw material. Notably, the rigid conformation and the sterically hindered ß-D-face of the molecule are advantageous for regioselective protection of the OH groups and stereoselective functionalization. Preparation of various biologically active compounds such as antibiotic macrolides has been approached starting from levoglucosan. Saccharification through rapid or vacuum pyrolysis of cellulosic biomass has also been proposed as a pre-treatment method for ethanol fermentation. Since the Pictet's report in 1918 [24], polymerization of levoglucosan has been studied extensively. Many kinds of polysaccharides have been prepared from polymerization of levoglucosan and its derivatives.

Yield of levoglucosan from cellulosic biomass is known to be influenced by various factors. Pyrolysis temperature and the inorganic impurities are the most important factors. Effective production of levoglucosan requires >300°C. Many papers have reported that only very small amounts of the inorganic impurities reduced the levoglucosan yield greatly, although the mechanism has not been clarified yet. As a factor relating to cellulose itself, the levoglucosan yield increases with an increasing crystallinity of cellulose. Some papers also indicate the influences of other constituent polymers in cellulosic biomass; Hosoya et al.[25] have reported that most of the identified volatile products from cellulose and lignin increased in their yields in pyrolysis of cellulose-lignin mixtures.

Mass- and heat-transfer efficiencies have also been discussed with the levoglucosan yield. The levoglucosan yield increases under vacuum conditions, since levoglucosan effectively vaporizes before suffering from the secondary reactions. Fast pyrolysis conditions, which are characteristic in rapid heating and quick recovery of the product vapour, are also preferable in production of levoglucosan.

Accordingly, the relationships between the pyrolysis condition and the levoglucosan yield are well documented. However, it has not been discussed how coexisting products from cellulose and other cellulosic biomass affect the recovering process of levoglucosan. Levoglucosan is reported to be stabilized up to 350°C in some aromatic substances with high π-electron densities probably through complexation with the CH/π interaction. Such alternation of the reactivity may be included in pyrolytic production of levoglucosan. Understanding the secondary decomposition behaviour in the presence of other pyrolysis products will be useful to improve the pyrolytic production of levoglucosan.

For pyrolysis of biomass a widely variety of reactor configurations were studied [7,8]. Fluid beds offer robust and scalable reactors, but the problem of heat transfer at large-scales in not yet proven. Circulating fluid beds and transported beds may overcome the heat transfer problem but scaling is not yet proven and there is an added problem of char attrition.

Mechanical devices such as ablative, rotating cone and screw reactors offer advantages of compactness and absence of fluidizing gas, but my suffer from scaling problems and always the problems associated with moving parts at high temperature.

The liquid bio-oil products has the considerable advantage of being storable and transportable as well as the potential to supply a number of valuable chemicals.

There are specific challenges facing pyrolysis products that relate to technology, product and applications including :

- Cost of bio-oil, which is 10% to 100% more than fossil fuel.
- Availability : there are limited supplies for testing and development of applications.
- Lack of standards for use and distribution of bio-oil and inconsistent quality inhibits wider usage.
- Incompatibility with conventional fuels.
- Users are unfamiliar with bio-oils, and dedicated fuel handling systems are needed.

5. Fuels and chemicals from polymer wastes

The goal of our research [9-23] was to study chemical and feedstock recycling of polymer waste. We have studied:

- if the oils/waxes obtained from thermal cracking of individual and mixed polymers are able to produce valuable fuels (automotive gasoline and diesel fuel)
- if it is possible to obtain low molecular alkenes (ethene and propene) of solutions (oil/wax
- in heavy naphtha) during copyrolysis

Individual and mixed polymers are suitable for thermal cracking in inert nitrogen atmosphere at 450°C. Gaseous, liquids (oils/waxes) and products are produced (Fig. 3).

The prevailing gaseous hydrocarbons from thermal cracking of individual and mixed polymers are C_3 (propane, propene), C_2 (ethane, ethane), C_4 (butane, 1-butene a methylpropene) a C_5 (pentane, 1-pentene). Formation of aromatics presented in gas is low or aromatics are not present. In the case of thermal cracking of simulated plastic waste is the production of aromatics low too.

The polyethylene oils/waxes are composed predominantly of linear alkanes and 1-alkenes but polypropylene oils/waxes are composed also of branched alkanes and alkenes. The addition of polypropylene to the individual polyethylene (LDPE, LLDPE, HDPE) influences the product distribution in oils/waxes and gases. Besides linear alkanes and alkenes are present also branched alkanes and alkenes in mixtures.

Oils/waxes are suitable for distillation. The first fraction obtained from each feedstock was distilled at atmospheric pressure up to the temperature of 180°C corresponding to the gasoline. The second fraction underwent a vacuum distillation, which was stopped at the temperature of 190°C that corresponds to the temperature of 330°C at the atmospheric pressure. This fraction corresponds to the diesel fuel.

Unsaturation of oils/waxes is represented by value of bromine number. The values of bromine numbers for distillates (gasoline and diesel fuel) obtained by distillation of oils/waxes are higher than for original oils/waxes. They contain higher amount of unsaturated hydrocarbons. It is interesting that values of bromine numbers of distillates and oils/waxes of LDPE/PP (1:1) are similar as for individual polypropylene. The presence of aromatics in gasolines and diesel fuels is low or they are not present. Another advantage of obtained fractions is that they not contain sulfur.

The octane number is a measure for quality of gasoline. The value of octane numbers for gasoline (RON) is high despite low amount of aromatics. The value of octane number (RON) for original gasolines is higher than for hydrogenated gasolines. The polypropylene is exception. Octane numbers (RON) for original gasoline of polyethylenes are about 81 to 82 units and for hydrogenated naphtha fraction are from 67 to 71 units. Octane numbers (RON) of polypropylene is about 93 before hydrogenation and after hydrogenation.

The value of diesel index increases after hydrogenation of diesel fuel. Diesel index for original diesel fuels (from 73.7 to 75.6) and hydrogenated diesel fuels (from 98.2. to 104.9) presents excellent combustion properties. The amount of aromatics is low.

Oils/waxes obtained by thermal cracking of polymers are better dissolving in the liquid petroleum fraction of heavy naphtha because they are present in oil/wax in the form of smaller molecules. Thanks their composition (alkanes, alkenes, the small amount or no amount of aromatics) they are suitable as feedstock for pyrolysis/co-pyrolysis. The presence of PET, PVC and PS do not worsen the quality of oils/wax.

The addition of oils/waxes influences yields of ethene and propene during co-pyrolysis in the presence of steam. The yields of ethene and propene are higher or comparable with the yields of virgin heavy naphtha. The finding proving that the solution of LLDPE/LDPE/PP/HDPE/PVC/PET/PS is able to provide high yields of propene and similar or higher yields of ethene in the comparison with virgin heavy naphtha, at both temperature levels is rather positive. The yields of propene are similar with yields of solution of HDPE with naphtha. We have confirmed that even if the solution contains PET, PVC and PS is suitable for co-pyrolysis (Fig. 2).

The addition of oils/waxes influences the formation of coke as also the amount and composition of pyrolysis gas and liquid during co-pyrolysis of solution (oil/wax in naphtha) in sever reaction conditions (without steam). Heavy naphtha was used as "baseline". The amount of produced coke obtained from pyrolysis of heavy naphtha was compared to the amount of produced coke obtained from co-pyrolysis of solutions.

Shape of kinetic curves of formed coke has the same trend for all feedstocks. Kinetics of coke deposition confirms that the coking rate is the highest stage in initial stage of experiment . The catalytic influence of metal reactor surface causes high initial coking rates that evidence the coking is carried out on clean reactor surface. The high initial coking rate depends on properties of feedstock too. The initial contribution of coke deposition

for different feedstock is minimal. The differences in formed amount of coke are evident in other stages. The formation of carbon oxides is higher under co-pyrolysis conditions.

Oil/waxes obtained in thermal cracking of polymers (individual, mixed polymers, polymers simulating the composition of plastic waste) in 10 and 15 mass % amount in heavy naphtha are suitable as feedstocks for co-pyrolysis at 820°C which is evident from the formed depositions of coke.

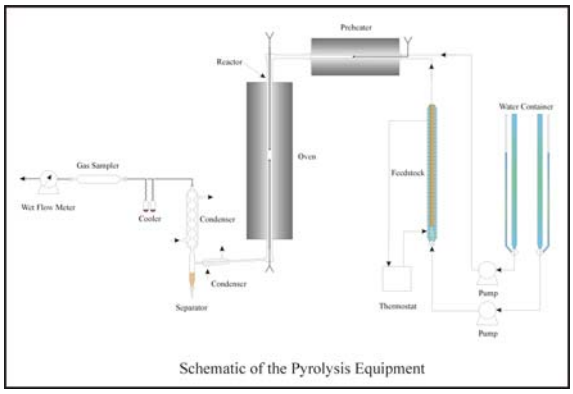

Fig. 2. Schematic of the flow pyrolysis laboratory equipment

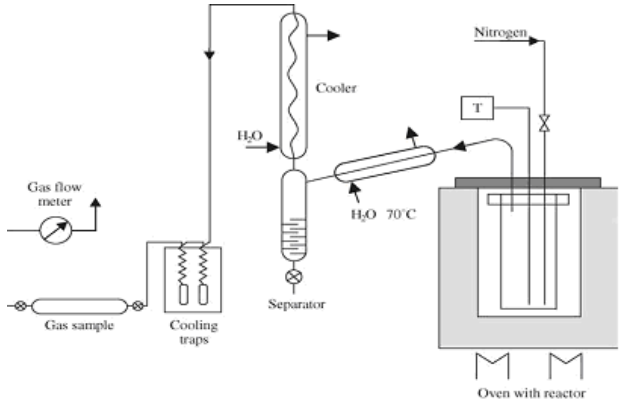

Fig. 3. Schematic diagram of the thermal decomposition reactor

Obtained results suggest the possibility of polymer recycling using co-pyrolysis. The amount of formed coke obtained in co-pyrolysis for 10 or 15 mass % solutions doesn't vary a lot in comparison to the amount of formed coke obtained from pyrolysis of individual heavy naphtha. Adding 10 mass % (and more) of waste polymers to virgin heavy naphtha can spare a substantial amount of this valuable liquid raw material.

6. Fuels and chemicals from used tyres

Used tyres are among the waste materials which represent problematic wastes on the one hand and a valuable potential as secondary raw materials on the other hand. As the European Union intends to limit the amount of organic matter being landfilled in the near future, the only disposal alternatives left for rubber wastes will be incineration and recycling.

While incineration utilizes the energetic content of the wastes, recycling may partially conserve their chemical structure and therefore possibly represent a better ecological approach.

In the recent years, about 40% of tire and rubber waste was incinerated, 17% reused or exported to countries outside the European Union, 9 % used as recyclate and 20 % for other uses. Due to the irreversible chemical structure of the rubber, a primary or secondary recycling is only possible to a limited extent. Research in the field of chemical recycling of rubbers by pyrolysis has focused on scrap tires as the most important rubber waste. Apart from scrap tyres, rubbers for non-tire applications (technical rubbers represent an important disposal problem.

Whole tyres were pyrolyzed successfully on laboratory and technical scale in flow reactor according Deep Scavenger Steam Cracking process or Steam Cracking Activation process (DSSC/SCA), which has been developed by DRON-Sklady, Mliečany, Slovakia. The laboratory batch reactor has been used for the decomposition of used tyres (Fig. 3)

The design of the pilot plant reactor throughput of 200 kg/h used tires is shown schematically in Fig. 4. The view of the technological unit reactor a throughput 15 000 t/year is shown in Fig. 5.

At a temperature from 400 to 700°C, gas (18% mass), oil (35% mass) with a high content of BTX aromatics and d, l-limonene, coke (40% mass) and iron-steel (7% mass) were yielded.

The pyrolysis oil shows a high heating value of about 50 $MJ.kg^{-1}$. Pyrolysis gases are composed from methane, C_2-C_5-hydrocarbons, hydrogen, carbon monoxide, carbon dioxide and hydrogen sulphide. Gases are comparable with the natural gas and are therefore a good source for heating plant. Fuel producing energy for the tyre processing plant or energy inputs for other purpose.

Oil fraction is composed from aromatic hydrocarbons, polyaromatic species, limonenes, aldehydes, ketones and carboxylic acids. Oil fraction has variable application, particularly used as a fuel producing energy.

Coke has increased char surface area with the temperature reaction and rate of heating obtained up to 70-80 m^2/g. Surface areas are comparable with raw carbon black which is used in tyre manufacture. Carbon black as the most valuable fraction can be reused after activation with steam as filler material in the technical rubber production. Pyrolysis char contains higher proportion of ash and has large particle size, which make this product an alternative to carbon black. Coke has a heating value 28-34 $MJ.kg^{-1}$. Iron material is high quality feedstock waste for steel production.

Fig. 4. The design of the pilot plant reactor

Fig. 5. The view of the technological unit in Mliečany

Advantages of DSSC/SCA process [23] :

- New effective technology of thermal cracking of used tyres with steam activation,
- Full exploitation and processing of rubber waste and used tyres,
- Total material conversion of rubber waste and used tyres,
- Own energy supplies,
- High potential in the nearest future.

7. Conclusions

For pyrolysis of biomass and wastes widely variety of reactor configuration were studied. New effective technology of thermal cracking of used tyres with steam activation was developed at Slovak University of Technology in Bratislava and applied in the DSSC/SCA process in Mliečany, Slovakia with total plant capacity approach 15 000 t/year.

The liguid bio-oil from biomass and pyrolysis oil from polymer wastes have the considerable advantage of being storable and transportable as well as the potential to supply a number of valuable fuels and chemicals. The cost of bio-oil is 10% to 100% more than fossil fuel.

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