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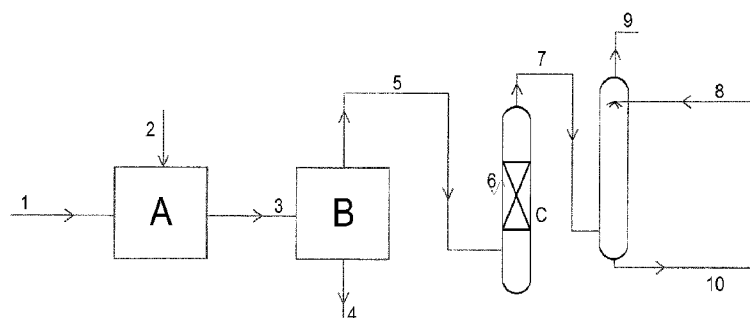


Fig. 1.

(57) Abstract: Aromatic compounds are prepared from a feed stream comprising biomass or a mixture of biomass and synthetic polymer in a process, comprising: a) subjecting the feed stream to a pyrolysis treatment in the presence of a cracking catalyst to yield a vaporous fraction comprising hydrocarbons with olefinic unsaturation and oxygen containing organic compounds and coke-laden cracking catalyst; b) separating the vaporous fraction from the coke-laden cracking catalyst; c) contacting the vaporous fraction with a second, aromatization catalyst in a conversion treatment to yield a conversion product comprising aromatic compounds; and d) re-covering aromatic compounds from the conversion product, wherein the cracking catalyst is a naturally occurring material, selected from the group consisting of inorganic salts, refractory oxides, minerals, industrial rock and mixtures thereof.



PROCESS FOR THE PREPARATION OF AROMATIC COMPOUNDS

The present invention relates to a process for the preparation of aromatic compounds from a feed stream comprising biomass or mixtures of biomass and synthetic polymer.

Aromatic compounds such as benzene, toluene, xylenes and naphthalenes, represent valuable starting materials for a large number of applications. Mixtures of such compounds can be found in aromatic fuels, including gasoline. Benzene may further be used as chemical intermediate, e.g. in the production of ethylbenzene, cumene and cyclohexane. Toluene has found application as a solvent, e.g. for paints, printing ink and glues. It is also used as chemical intermediate in the preparation of toluene diisocyanate, which is a starting material for the production of polyurethane foams. Further it may be used in its disproportionation to benzene and xylenes. p-Xylene is used in the preparation of terephthalic acid, which is a monomer for several plastics, such as aramid and polyesters, such as polyethylene terephthalate (PET). o-Xylene is mainly used in the production of plasticizers for PVC. The main market for naphthalene resides in the preparation of phthalic acid.

Currently, these aromatic compounds are produced via refinery processes of fossil fuels. Common processes include steam cracking, steam reforming and catalytic reforming. In order to arrive at a more environmentally friendly and sustainable production of these aromatic compounds, research has been carried out in identifying different, more sustainable starting materials for the production thereof. Such suitable starting materials include refuse and biomass and mixtures thereof.

In US 5,504,259 a process is described wherein biomass or refuse-derived fuel is converted into reformulated gasoline components, in particular into ethers and alcohols. According to this process the biomass or refuse-derived fuel is subjected to a fast pyrolysis reaction whereby volatile intermediate vapors are formed. These vapors are fed to a catalytic cracking reactor and thus cracked to low molecular weight hydrocarbons. The hydrocarbons obtained comprise aromatic byproducts. The gaseous components and the small amount of benzene formed are then compressed. The benzene is subsequently alkylated to yield alkyl benzenes, which are suitable fuel components. The main products formed in the process are olefins, which may be converted to oligomers, to ethers and/or to alcohols. The process only results in a very low yield of aromatic compounds. In J. Diebold and J. Scahill: Biomass to Gasoline, in Pyrolysis Oils from Biomass (30 September 1988, ACS, Washington DC., part 376, pages 264-276) a similar process is described.

A higher yield of aromatic compounds is claimed to be obtainable in a process, described in US 2012/0203042. This patent document describes a process wherein biomass is subjected to a catalytic pyrolysis treatment. The catalytic pyrolysis treatment is conducted

at a temperature of 500 to 1000 °C in the presence of a catalyst that may be selected from a range of zeolitic catalysts. The products obtained in the catalytic pyrolysis treatment may be separated into an olefin fraction and a second fraction. The olefin fraction is recycled to the catalytic pyrolysis treatment, whereas the second fraction is passed to a product reactor wherein hydrocarbon products may be further converted, e.g. to aromatic compounds. The subsequent reaction of hydrocarbon products to aromatic compounds takes place in the presence of a zeolitic catalyst. After the reaction, the catalyst is regenerated by exposure to oxygen, and subsequently recycled to the catalytic pyrolysis treatment. The described method implies that the same catalyst is used in the catalytic pyrolysis treatment and in the product reactor.

The process according to US 2012/0203042 therefore describes a one-step catalytic pyrolysis process that is followed by a conversion of hydrocarbons produced into aromatics over zeolitic catalyst. This process has the drawback that the zeolitic catalyst may get severely contaminated with coke and inorganic material during the catalytic pyrolysis. The inorganic material originates from the biomass feedstock used (cf. C. Dorado, C.A. Mullen, A.A. Boateng, ACS Sustainable Chem. Eng., 2014, 301-311, and Mechanisms of catalyst deactivation, C.H. Bartholomew, Applied Catalysis: General 2001, 17-60). The contamination will have an effect on the activity of the catalyst in the aimed conversion of hydrocarbons to aromatic compounds and, furthermore, it will shorten the lifetime of the catalyst. One possibility to regenerate the catalyst resides in contacting the thus deactivated catalyst with oxygen in order to burn off the coke. Although such regeneration of the catalyst by reaction with oxygen may remove at least part of the coke or carbon residues, it will definitely not remove inorganic material. Rather, the inorganic material will remain firmly deposited on the catalyst. Such deposits may require the replacement of the catalyst. As a result, this may add to the costs and may reduce the time during which the reaction is on-stream.

In WO 01/05908, a waste feed is catalytically pyrolyzed in the presence of a first zeolitic cracking catalyst (HZSM-5) to produce a gaseous phase which is introduced into a fixed bed to perform a second catalytic reaction with a catalytic mixture comprising a zeolitic aromatization catalyst (ZSM-5). The process thus uses a two-step catalytic process. The splitting of the process enables optimization of both the cracking phase as well as the aromatization phase. Because the feed stream is composed of waste plastics and/or heavy oil, the catalysts do not run the risk of suffering from contamination with inorganic material.

In US 2011/283601 a biomass feed stream is used. Biomass is subjected to catalytic pyrolysis in the presence of a zeolite or clay catalyst in a pyrolysis reactor. The vapor stream is condensed and the non-condensable gases containing olefins are separated from the bio-oil and subsequently aromatized in the presence of a zeolite catalyst. US 2011/283601 is aimed at a high production of bio-oil. The condensation step is believed to be susceptible to

secondary reactions which decrease the yield of aromatic compounds. Furthermore, condensing and then reheating the gases is energetically unfavorable.

WO 2009/111026 also describes a catalytic pyrolysis process. In one of the embodiments a biomass feed stream is converted into aromatics in a two-step catalytic process, where catalytic pyrolysis and upgrading of the obtained vapors take place in different reactors. However, as described above, the relatively expensive zeolitic catalysts used in the first step of the process suffer from contamination with coke and inorganic residues. Replacement of the catalyst adds to the costs of the process.

It is an object of the present invention to provide a process for the synthesis of aromatics from biomass wherein the above-mentioned drawback of contamination of an expensive catalyst is overcome. It has been found that the application of a two-step catalytic process wherein different catalysts are used in the different steps, provides a solution to this problem. The first (cracking) catalyst may then be chosen to be relatively cheap, but also very effective. An optimum balance of cost and effect can be sought. The first catalyst influences the amount and the composition of the vapor phase that is formed.

Accordingly, the present invention provides a process for the preparation of aromatic compounds from a feed stream comprising biomass or mixtures of biomass and synthetic polymer, the process comprising:

- a) subjecting the feed stream to a pyrolysis treatment in the presence of a cracking catalyst to yield a vaporous fraction comprising hydrocarbons with olefinic unsaturation and oxygen containing organic compounds and coke-laden cracking catalyst;
- b) separating the vaporous fraction from the coke-laden cracking catalyst;
- c) contacting the vaporous fraction with a second, aromatization catalyst in a conversion treatment to yield a conversion product comprising aromatic compounds; and
- d) recovering aromatic compounds from the conversion product,

wherein the cracking catalyst is a naturally occurring material, selected from the group consisting of inorganic salts, refractory oxides, minerals, industrial rock and mixtures thereof.

Naturally occurring materials, such as inorganic salts, refractory oxides, minerals and industrial rock do not require extensive synthesis. They are readily available and are therefore relatively cheap. They are also easily disposable. Examples of such catalysts include naturally occurring inorganic salts, refractory oxides, minerals and/or industrial rock, in which optionally ions can be exchanged in a simple ion exchange process. Synthetic zeolites such as HZSM-5 and ZSM-5 on the other hand are a clear example of catalysts that are not cheap, as they require specialized synthesis.

The skilled person may select the most suitable cracking catalyst dependent on the starting material used in the feed stream, whereas he does not have to take into account any decreased activity in the subsequent conversion of the vaporous fraction. In the pyrolysis of the feed stream in first catalytic pyrolysis step coke and inorganic material is deposited onto

the cracking catalyst. Therefore, the skilled person may select the most suitable catalyst for the aromatization of the vaporous fraction, without fear that the aromatization catalyst will be affected by the deposition of inorganic material. Thus, undue contamination of the aromatization catalyst with inorganic mineral material is avoided.

Contrary to US 2011/283601 in the process of the current invention after step b) the vaporous fraction is contacted with a second, aromatization catalyst in step c). Step c) directly follows step b), i.e. there is no condensation and reheating step in between steps b) and c).

As indicated above, the pyrolysis step a) of the present invention is carried out by contacting the feed stream with a cracking catalyst. In the present process, the skilled person has the option to select the most suitable catalyst for the pyrolysis treatment. He may consider different types of catalysts and take into account the nature of the feed stream. The cracking catalyst according to the present invention may therefore be amorphous or crystalline. In order to facilitate the pyrolysis reaction the cracking catalyst is preferably selected from the group consisting of acidic or alkaline inorganic materials, more preferably from acidic inorganic materials from the above defined group of naturally occurring materials. These inorganic materials may be refractory oxides. Refractory oxides are metal oxides that can sustain high temperatures. Such oxides include the oxides of aluminium, silicon, magnesium, zirconium, titanium, chromium and other metals. Crystalline inorganic materials include aluminosilicates, silicon-aluminium phosphates, silicalite, other natural zeolites and clays.

The cracking catalyst is preferably selected from acidic or alkaline inorganic materials and combinations thereof. Alkaline refractory oxides include magnesium oxide and combinations of magnesium oxides with chromia or with calcium oxide, which therefore constitute suitable cracking catalysts. Suitable acidic refractory oxides include silica-alumina.

The cracking catalyst is not restricted to the use of silica-alumina. As stated above, other amorphous and crystalline catalysts of natural origin may also be used. Crystalline, e.g. zeolitic, catalysts may also be used. Dependent on the desired cracking activity, the skilled person may select the most suitable catalyst. He may vary the silica-alumina ratio, he may vary the structure or pore size distribution in the catalyst, and he may vary the level of presence of elements other than silicon and aluminium. The silica-alumina ratio may vary from about 1 to 100. The other elements may be alkali metals, that can be exchanged for e.g. protons, thereby providing the desired acidity, but also other metal and non-metal elements that are incorporated in the crystalline structure. Examples thereof include silicoaluminophosphates (SAPOs), iron silicates, gallium silicates and combinations thereof. Alternatively, the catalyst may be improved by the addition of other, catalytically active materials, in particular metals. The metals may be incorporated into the catalyst by means of various methods, including impregnation and kneading. The metals include Group 6, 7 or 8

metals, including noble metals. Suitable examples are iron, nickel, copper, cobalt, tungsten, molybdenum, platinum, palladium, ruthenium, rhodium and combinations thereof.

Preferably, the cracking catalyst is selected from the group consisting of amorphous and crystalline silica-alumina-comprising materials, and combinations thereof. Since the cracking catalyst may be amorphous or crystalline and the catalyst is preferably acidic, the cracking catalyst is suitably selected from amorphous or crystalline silica-alumina-containing inorganic materials. One very suitable cracking catalyst is amorphous silica-alumina. It is surprising that amorphous silica-alumina is such a preferred catalyst, since US 2012/0203042 teaches that when silica-alumina is used in the pyrolysis-conversion process of glucose according to this patent document, primarily coke is produced with a very low production of aromatics. It has now been found that when silica-alumina is used as cracking catalyst in the pyrolysis an excellent vaporous fraction is obtained that can advantageously be used for the production of aromatic compounds with a second, aromatization catalyst.

Preferably, the cracking catalyst is bentonite. This material has shown to result in a higher yield of aromatics as compared to other amorphous silica-aluminas.

In the process of the present invention the feed stream is treated in a pyrolysis zone in the presence of a cracking catalyst. The difference with the pyrolysis treatment in US 5,504,259 and Diebold et al. resides in that in this known process no catalyst is used. The pyrolysis reaction takes place under the influence of heat only. In the known process of US 5,504,259 the pyrolysis reaction is conducted at a temperature of about 625 °C. US 5,504,259 discloses that the pyrolysis zone may comprise a vortex reactor.

Utilization of a catalyst in the pyrolysis step influences the yield of the vaporous fraction and allows thus the skilled person to produce significantly higher amounts of aromatics in the subsequent aromatization step. The catalytic pyrolysis reaction according to US 2012/0203042 may be carried out at a broad temperature range of 300 to 1000°C. The reaction pressure in this known process may be as low as atmospheric, and may be up to about 4 bar. The reaction conditions of the pyrolysis step a) in the present process may be comparable to those of the process according to US 2012/0203042, and are suitably a temperature in the range of 450 to 1000 °C, preferably from 500 to 600 °C, and a pressure of 1 to 6 bar, preferably from 1 to 4 bar.

The pyrolysis treatment of step a) may be carried out in a variety of reactors. Such reactors include a continuous stirred tank reactor (CSTR), a fixed bed reactor, a moving bed reactor, an auger reactor, a screw conveyor reactor, an entrained flow reactor, a rotating cone reactor and a fluidized bed reactor. Since the cracking catalyst tends to receive deposits of coke and other carbon residues it is preferred to employ a reactor that allows easy, and preferably continuous, regeneration. Therefore, the use of a CSTR, moving bed, an auger reactor, a screw conveyor reactor, an entrained flow reactor, a rotating cone reactor or fluidized bed reactor is preferred over the use of a fixed-bed reactor. The effluent from such

reactors can be separated and the catalyst may be passed to a regenerator and recycled to the pyrolysis treatment. Reactors that allow for a relatively short contact time and for intense mixing of the components of the feed stream with the cracking catalyst and for a continuous recirculation of regenerated catalyst to the pyrolysis zone are most preferred. Since this is the case for an auger reactor and a fluidized bed reactor, these reactors are particularly preferred.

When the cracking catalyst is contaminated with a level of deposits that cannot be removed by regeneration it may be replaced by fresh cracking catalyst. To that end a bleed stream of deactivated catalyst may be provided and a make-up stream of fresh catalyst. Alternatively, the catalyst may be used once or only a number of times, say 1 to 100 cycles. In such a situation, the pyrolysis may be conducted in a moving bed reactor, wherein the catalyst slowly moves through the reactor and the used catalyst is either discharged, or passed to a regenerator for a few times and discharged after a few cycles. This is also applicable to a pyrolysis reaction in an auger, screw conveyor, entrained flow reactor or fluidized bed reactor. Also in case of these reactor types it may be desirable to operate with a bleed stream of deactivated catalyst and a make-up stream of fresh catalyst.

In a preferred process according to the present invention the coke-laden cracking catalyst is regenerated by contacting the coke-laden cracking catalyst with oxygen to yield a regenerated cracking catalyst. The regeneration also yields heat that can be used to provide the required thermal energy in the catalytic pyrolysis treatment. Preferably, the regenerated cracking catalyst is recycled to the pyrolysis treatment of step a). The regeneration of coke-laden cracking catalyst may be carried out in a similar fashion as the well-known regeneration in fluid catalytic cracking processes.

The separation of the vaporous fraction and the coke-laden cracking catalyst may be carried out in any known method to separate a vapor from a solid. Such methods include filtering, electrostatic separation and separation by inertia. In the present process filtering is not preferred since this generally does not allow for separation at pyrolysis temperatures. Electrostatic separation is feasible, but tends to be cumbersome. It is preferred to separate the vaporous fraction from the coke-laden cracking catalyst using inertia. This technique is based on the recovery of solid particles by a change of direction of the solids-containing gas flow. This can be achieved by static separators. However, this is commonly better obtained by using centrifugal forces, e.g. in one or more cyclones. Techniques that are commonly used in fluidized catalytic cracking are available for an efficient separation of the vaporous fraction and the coke-laden cracking catalyst. Separation with one or more cyclones may be followed by electrostatic separation, if found desirable.

The vaporous fraction thus obtained is subsequently used for the conversion into aromatic compounds. The vaporous fraction obtained by catalytic pyrolysis according to the invention is very suitable for such a conversion since it tends to comprise hydrocarbons with

olefinic unsaturation. It has been found that the vaporous fraction suitably further comprises oxygen-containing organic compounds. These various oxygen-containing compounds are suitably one or more compounds selected from phenols, aldehydes, ketones, furan derivatives that may optionally be partially hydrogenated, and mixtures thereof. These latter compounds that already contain a certain level of unsaturation appear to be easily converted into aromatic compounds.

It will be understood that the composition of the vaporous fraction to some extent depends on the nature of the feed stream and the conditions applied. It has been found that good results are obtainable with feed streams that comprise biomass selected from the group consisting of agricultural waste, plants, wood, and combinations thereof. The feed stream suitably comprises organic material such as, glucose, maltose, starch, cellobiose, cellulose, hemi-cellulose, other polysaccharides, lignin, sugar cane bagasse, lignocellulosic materials (e.g., wood chips or shavings, lignocellulosic biomass, etc.), food waste, animal waste, manure and corn stover. Also partially decayed vegetation, such as peat or even lignite can be used as biomass feed material in the process of the present invention. Other examples of suitable materials include, for example, plastic waste, recycled plastics and other polymers in a mixture with biomass.

Surprisingly it has been found that when the feed stream comprises a blend of synthetic polymer and cellulose-containing material, the yield of aromatic compounds is synergistically enhanced. In particular when the synthetic polymer is a polyester, such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN), the results are excellent. Therefore, the skilled person may opt for a combination of blending a separate stream of synthetic polymer, such as recycled PET, with a carbohydrates-containing stream, such as cellulose containing biomass. This is also evident from the results of Li et al. (Applied Catalysis A: General, 455, 114), in which aromatic production is improved by co-feeding low-density polyethylene with cellulose.

It will be realized that the feed stream may contain significant amounts of water. Therefore it may be advantageous to dry the feed stream to water levels that are regarded as suitable. Typically, the water level in the feed stream is brought to a level of at most 10%wt, based on the weight of the feed stream. Preferably, it is ensured that the feed stream contains at most 5%wt, more preferably at most 2%wt water, based on the feed stream. The desired level of water may be achieved by subjecting the feed stream to be to a drying treatment. Similar to the drying treatment that has been described in US 2012/0203042 the drying may be established in an oven that is heated to at least about 80 °C, through which the feed stream to be treated, is passed continuously, semi-continuously or periodically. When the drying is established in a periodical batch-wise manner, the feed may also be subjected to sub-atmospheric conditions to facilitate the drying process.

It has now surprisingly been found that a pre-treatment of the feed stream in the presence of a catalyst has a beneficial effect on the yield of aromatic compounds after the conversion step c) of the present process. Therefore, the feed stream is preferably subjected to a pre-treatment before being subjected to the pyrolysis treatment in step a). The pre-treatment suitably comprises a heating step at a temperature in the range of 200 to 350 °C, preferably from 225 to 300°C. Very good results have been obtained with a pre-treatment at which the feed stream was subjected to a heat treatment of about 275 °C. The duration of the pre-treatment may vary within wide ranges. It is preferred to have the duration last as short as feasible. Therefore, the feed stream is suitably subjected to the pre-treatment for a period of 1 to 45 min, preferably from 2 to 15 min. Such a short treatment hardly adds to the cost or hinders the carrying out of the process, whereas the yield of aromatic compounds is enhanced. The heating step may take place in ambient atmosphere, which means at ambient pressure and also in the presence of air.

The pre-treatment may be part of the process according to the present invention. However, it may also be employed in other processes, including the process according to the prior art. Hence, in a broad context, the present invention also provides a process for pyrolysing a feed stream comprising biomass or a mixture of biomass and synthetic polymer, comprising, subjecting the feed stream to a pre-treatment in the presence of a cracking catalyst, and subsequently subjecting the thus pre-treated feed stream to a pyrolysis treatment in the presence of the cracking catalyst.

When the vaporous fraction has been separated from the coke-laden catalyst the coke-laden catalyst may be disposed. Alternatively, the catalyst may be suitably regenerated by contact with an oxygen-containing gas to burn off the coke and regenerated catalyst may be recirculated to the pyrolysis treatment in step a). The vaporous fraction is subsequently contacted with the second, aromatization catalyst in the conversion step c). The second catalyst is different from the coke-laden catalyst from which the vaporous fraction has been separated. Preferably, the second, aromatization catalyst is a zeolitic catalyst, suitably selected from aluminosilicates, SAPOs, silicalites and combinations thereof. It has been found that the second, aromatization catalyst preferably is acidic. The acidity may be influenced by the structure of the aluminosilicate and also by the ratio between silicate moieties and aluminate moieties in the aluminosilicate. The acidity may e.g. be accomplished by ion exchange of the second, aromatization catalyst with ammonium salts and subsequent calcination thereof. The silica-alumina ratio (SAR) is relevant for the potential acidity of the second catalyst. At a low SAR and if virtually all the active sites have been rendered in the H^+ form, the resulting catalyst is very acidic. It will be evident that the acidic sites on the aluminosilicates and the variation in SAR will enable the skilled person to determine what catalyst performs optimally for the relevant feed streams, reaction conditions and product slate. Suitable SARs include those in the range of 5 to 100, preferably, from 10 to 80, more

preferably from 25 to 60. Another feature that may play a role in the performance of the present catalyst is the pore diameter. It has been found that particularly good results are obtained if the pore diameter of the catalysts is in the range of 4.5 to 6.5 Å, preferably from 5 to 6 Å. Although the second catalyst may be a SAPO, the second catalyst is preferably a zeolite, that is selected from the group consisting of ZSM-5, ZSM-11, ZSM-35, ZSM-23, ferrierite, zeolite beta, zeolite Y, zeolite X, mordenite, zeolite A, IM-5, SSZ-20, SSZ-55, MCM-22, TNU-9 and combinations thereof.

As indicated above, the acidity of the second, aromatization catalyst plays a role in the conversion of the vaporous fraction. The acidity may be related to the silica alumina ratio of the catalyst when the second, aromatization catalyst is a zeolitic catalyst. When the catalyst is a zeolitic catalyst also the pore size of the zeolite catalyst is a factor in the process according to the present invention. Preferred pore diameters are those above. A preferred catalyst comprises a H-ZSM-5 zeolite with a silica-alumina ratio in the range of 15 to 100, preferably of about 25-60, since such H-ZSM-5 is most optimal for production of aromatics.

The conversion treatment is suitably carried out at a temperature in the range of 300 to 1000 °C. Relatively high temperatures, such as 450 to 650 °C are preferred since they tend to increase the formation of aromatic compounds from the vaporous phase. The pressure suitably ranges from 1 to 4 bar. In the conversion treatment the catalyst is suitably present in a weight ratio of feed to catalyst in the range of 1:1 to 1:20.

According to US 2012/0203042 the use of silica-alumina is stated to result in primarily coke production. Therefore, the skilled person will be deterred from using amorphous silica-alumina in the conversion to aromatics. The present inventors have also found that the use of amorphous silica-alumina resulted in a lower yield of aromatic compounds, compared with the use of crystalline zeolites. It is therefore surprising to find that when a combination of a zeolitic catalyst and silica-alumina is being used, the yield on aromatic compounds is synergistically higher than would be expected on a proportional basis. The advantage of the combination of these types of catalysts may be achieved by employing a physical mixture of zeolite particles and silica-alumina particles. Alternatively, the zeolite may be comprised in an amorphous binder. Thus the second catalyst may suitably comprise an amorphous binder in addition to a zeolite. The amorphous binder gives the particle thus obtained strength and provides a certain particle size to the catalyst particles. Therefore, the amorphous binder can suitably be selected from inorganic refractory oxides, in particular alumina, silica, silica-alumina, titania, zirconia and mixtures thereof. Since in addition to the provision of mechanical strength a synergistic effect can be obtained when the amorphous binder is silica-alumina, such a binder is particularly preferred.

When a binder is used, the amount of the binder in such combinations may vary within wide ranges. Suitably the amount of amorphous binder in a zeolitic second catalyst is in the range of 30 to 80 %wt, preferably, 40 to 70 %wt, based on the weight of the zeolite and the

amorphous binder. Such a ratio not only provides a particle with a satisfactory mechanical strength, but is also, in the case of silica-alumina, provide the synergistic effect of an increased aromatic compound yield, compared to the proportionally expected yield.

As in the case of the pyrolysis treatment of step a) also the conversion treatment of step c) of the present invention may be carried out in a variety of reactors. Suitably, the present process is carried out as a continuous process. Thus the step c) of the present process may be carried out in a fixed bed. The vaporous fraction may in this case be passed through the bed in an up-flow or a down-flow direction. However, since the conversion to aromatic compounds may result in some coke deposition on the second catalyst a gradual deactivation may take place in such a fixed bed. Therefore, it is preferred to conduct the conversion treatment in a moving or fluidized bed. In a fluidized bed the catalyst is continuously added and passed in a fluidized way to an exit whilst being surrounded by vapors. The vapors comprise initially the vapors from the vaporous fraction, but they over time are converted to aromatic compounds. Then the catalyst is separated from the vapors and may then be passed to a regenerator where it is subjected to contact with an oxygen-containing gas to remove any coke that is deposited on the second catalyst. The skilled person will be familiar with the concept of catalyst regeneration in a fluid bed arrangement. The catalyst that is thus regenerated may, typically continuously, be recycled to the conversion treatment.

The conversion product is then subjected to a separation step to recover aromatic compounds. It is feasible to recover the various aromatic compounds separately. Alternatively, it is feasible to recover all aromatic compounds in one fraction. The desired level of fractionation will be adopted in accordance with the needs and uses of the aromatic compounds. The conversion product does not consist completely of aromatic compounds. It will contain some by-products, such as olefins. It is sometimes desired to recover the olefins separately from the aromatic compounds. Also other byproducts, such as alkanes, such as methane, hydrogen, carbon monoxide, carbon dioxide and water may be present. Therefore, the conversion product is preferably subjected to fractionation, yielding aromatic compounds as separate fraction or fractions, optionally one or more olefin fractions, and a residue. Preferably, the fractionation also yields an olefin fraction. The residue may be combusted to yield energy for the heating of the various feed streams and intermediate products. At least part of the one or more olefin fractions may be recycled to the conversion treatment. It is also possible to recycle at least part of the one or more olefins fractions to the pyrolysis treatment. Hence, at least part of the olefins fraction is suitably recycled to the conversion treatment, to the pyrolysis treatment or to both. Also in the process according to US 2012/0203042 part of the olefins produced is recycled to the pyrolysis treatment in order to benefit the pyrolysis. It is evident that at least part of the one or more olefins fractions may be recycled to either one of the pyrolysis treatment and the conversion treatment and to both.

Another preferred method for increasing the yield on aromatic compounds is constituted by the addition of extra reactants to the conversion treatment. Such extra reactants can suitably be selected from the groups consisting of extra olefins, alcohols, aldehydes, ketones, acids and combinations thereof. The extra reactants suitably have from 1 to 6 carbon atoms. Examples of suitable extra reactants include hydrogen, butane, isobutene, pentenes and hexenes, methanol, ethanol, propanol or isopropanol and hexanol, formaldehyde and acetaldehyde, acetone, methyl ethyl ketone, formic acid and acetic acid.

A suitable method for recovering the aromatic compounds from the conversion product is constituted by a method wherein the conversion product is passed into an extraction column. A liquid hydrocarbon is sprayed into the conversion product thereby cooling the conversion product and providing a solvent for the aromatic compounds. Oxygen-containing compounds, including water that may be formed during the process, easily separate from the mixture of conversion product and liquid hydrocarbon. In this way the aromatic hydrocarbons are recovered together with the liquid hydrocarbon. After separation of the liquid hydrocarbon phase that contains the aromatic compounds from the phase that comprises oxygen-containing compounds, including water, the liquid hydrocarbon phase is suitably subjected to fractionation to obtain the aromatic compounds.

Accordingly, the present invention also provides a method for recovering aromatic compounds from a vaporous stream that comprises the aromatic compounds and oxygen-containing compounds, such as the conversion product, which method comprises contacting the vaporous stream with a liquid hydrocarbon to obtain a hydrocarbon phase containing aromatic compounds, and an oxygen-containing compound phase, and separating the hydrocarbon phase from the oxygen-containing compound phase. The aromatic compounds can be suitably recovered from the hydrocarbon phase via any known method, including fractionation. The liquid hydrocarbon can be aliphatic, cycloaliphatic or aromatic. The use of aliphatic or cycloaliphatic hydrocarbons has the advantage that the separation of the aromatic compounds can be made and it can easily be determined what the yield of aromatic compounds from the feed is. If aromatic hydrocarbons are used as liquid hydrocarbon the advantage is that no extraneous products need to be used in the process. The aromatic hydrocarbons that are used for this purpose may be the product from the conversion earlier. That would mean that a fraction of the aromatic compounds that have been separated from the conversion product can be used to extract further aromatic compounds from the conversion product. That has the advantage that no additional fractionation to recover the extraction solvent, i.e. the liquid hydrocarbon, separately is needed. The liquid hydrocarbon is suitably selected from the hydrocarbons containing from 6 to 12 carbon atoms. The temperature and pressure can be selected by the skilled person according to his desires. Suitable temperatures include from 30 to 150 °C, and suitable pressures range from 1 to 6 bar.

The aromatic compounds that are recovered as products of the present process may be used for conventional applications. These include application as aromatic gasoline, but also as precursor for polymers, and chemical intermediates as explained above.

The invention is further illustrated by means of the attached drawings and Examples. In the drawing:

Figure 1 is a flow diagram of an embodiment of the method according to the invention;

Figure 2 displays the influence of the cracking catalysts on vapor composition; and

Figure 3 displays the results of catalytic pyrolysis and H-ZSM-5 (23) upgrading of pinewood.

Referring to figure 1, a feed stream containing biomass, or a mixture of biomass and synthetic polymer is passed into a pyrolysis reactor A via a line 1. To the reactor A also a stream of cracking catalyst is passed via a line 2. In the pyrolysis reactor A the cracking catalyst and feed stream are contacted with each other at pyrolysis conditions to yield a vaporous phase and a solid phase which consists of the cracking catalyst with coke residues deposited thereon. After the reaction the vaporous fraction and the coke-laden cracking catalyst are passed via a line 3 to a separator B. In B the vaporous fraction is withdrawn via a line 5 whereas the coke-laden catalyst by gravity drops to the bottom of separator B and is then withdrawn via a line 4. The coke-laden cracking catalyst may be recycled to the reactor A. It may also be subjected to regeneration by burning off of the coke from the cracking catalyst. It may also be used as landfill, e.g. after removal of the coke.

The vaporous fraction in the line 5 is passed to a second reactor C, where it is passed over a bed of aromatization catalyst 6 to be converted into aromatic compounds. The conversion product leaves the reactor C as a vapor via a line 7. Although reactor C has been depicted as a fixed-bed reactor it is emphasized that also a fluid bed reactor is feasible. In either case zeolitic aromatization catalyst may be removed from the reactor C. The conversion product is subsequently passed into an extraction column D where it is contacted with a liquid hydrocarbon stream that is sprayed into the column D via a line 8 that is provided with a nozzle or manifold. Due to the contact with the liquid hydrocarbon, the aromatic compounds in the conversion product condense and are withdrawn, together with other liquids, e.g. liquid oxygen-containing compounds, via a line 10. Any residual gases are discharged via a line 9 for further treatment and disposal (not shown). The liquid aromatic products, liquid hydrocarbon and liquid oxygen-containing compounds in the line 10 are separated from each other, e.g. by phase extraction and/or fractionation (not shown).

The invention will be further elucidated by means of the following examples.

Example 1.

In a series of experiments mixtures of pinewood (< 200 micron) and catalysts (ratio 1 :5, 2-5 mg of a homogeneous mixture) were subjected to catalytic pyrolysis with a cracking catalyst

(inert atmosphere (He), $T = 540\text{ }^{\circ}\text{C}$) in a tandem micro-reactor and the vapors obtained were subsequently (*ex situ*) up-graded in a second reactor containing H-ZSM-5(23) (80 mg, particle size 212-425 micrometers, $T = 550^{\circ}\text{C}$). The products obtained were analyzed by GC-MS and the amount of aromatics formed (benzene, toluene, xylenes) was calculated afterwards.

Figure 2 displays the influence of the cracking catalysts on vapor composition. It shows that the use of different cracking catalysts can significantly influence the composition of the vapor phase formed.

Figure 3 displays the results of catalytic pyrolysis and H-ZSM-5 (23) upgrading of pinewood. The amounts of BTX formed are relative to a blanc reaction (non-catalytic pyrolysis and H-ZSM-5 (23) up-grading). The figure clearly shows that the catalytic pyrolysis and the subsequent up-grading of vapors obtained with H-ZSM-5 (23) clearly distinguishes from the non-catalytic pyrolysis and up-grading (= blanc). Under identical conditions, depending on the catalyst used, approximately 20-25% higher yields of BTX were obtained.

Example 2.

In a series of experiments plywood sawdust with a particle size of 0.1 to 1.0 cm was subjected to pyrolysis in a pyrolysis reactor based upon auger reactor technology. The composition of the sawdust was 44.4 %wt cellulose, 19.0 %wt hemicellulose; lignin 29.7%wt, balance being water and inorganic salts. The catalytic pyrolysis was conducted with different catalysts; Catalyst 1 being an amorphous silica-alumina (Saint-Gobain NorPro catalyst SS61138) and Catalyst 2 being H-ZSM-5 with a silica to alumina ratio of about 23. Catalyst 2 consisted of the zeolite (70%wt) and an alumina (pseudoboehmite) binder (30%wt). Before use the catalysts were ground to a particle size of 160 to 650 micrometers, and mixed with quartz sand in a weight ratio of catalyst to sand of 1:3. The catalysts were used in a catalyst to sawdust weight ratio (C/S) of 2.5 or 5.0.

The catalytic pyrolysis steps were conducted at different temperatures and different catalysts/feed ratios for a period of up to 12 hr at atmospheric pressure. For comparison purposes, the amount of aromatic compounds for some experiments was determined after the pyrolysis step. In two-step processes the vaporous fraction that was obtained in the pyrolysis reaction was passed over a packed bed of Catalyst 2. The amounts of benzene, toluene and xylenes (BTX) were determined and calculated on the basis of the feed.

For clarity's sake the results of BTX are normalized, the BTX yield of experiment 3 being equal to 100% and the BTX yield of Catalyst 1 being zero %.

Reaction conditions and results are shown in Table 1.

Table 1

Exp. No.	Pyrolysis			Conversion			Relative BTX,
	Catal.	C/S	T, °C	Catal.	T, °C	Duration, hr	%
1	1	5.0	600	-	-	-	1
2	2	2.5	500	-	-	-	32
3	1	2.5	500	2	500	0.10	100

The results show that amorphous silica-alumina does not lead to any amount of aromatic compounds. However, H-ZSM-5 does yield some aromatic compounds in a catalytic pyrolysis process, but the yield is further increased in the process according to the present invention.

1. Process for the preparation of aromatic compounds from a feed stream comprising biomass or a mixture of biomass and synthetic polymer, the process comprising:

- a) subjecting the feed stream to a pyrolysis treatment in the presence of a cracking catalyst to yield a vaporous fraction comprising hydrocarbons with olefinic unsaturation and oxygen containing organic compounds and coke-laden cracking catalyst;
- b) separating the vaporous fraction from the coke-laden cracking catalyst;
- c) contacting the vaporous fraction with a second, aromatization catalyst in a conversion treatment to yield a conversion product comprising aromatic compounds; and
- d) recovering aromatic compounds from the conversion product,

wherein the cracking catalyst is a naturally occurring material, selected from the group consisting of inorganic salts, refractory oxides, minerals, industrial rock and mixtures thereof.

2. Process according to claim 1, wherein the cracking catalyst is an amorphous silica alumina.

3. Process according to claim 1 or 2, wherein the cracking catalyst is bentonite.

4. Process according to any one of the preceding claims, wherein the pyrolysis treatment in step a) is carried out at a temperature of 450 to 1000 °C and a pressure of 1 to 6 bar.

5. Process according to any one of claims 1 to 4, wherein the pyrolysis treatment in step a) takes place in a fluidized bed or an auger reactor.

6. Process according to any one of claims 1 to 5, wherein the coke-laden cracking catalyst is regenerated by contacting the coke-laden cracking catalyst with oxygen to yield a regenerated cracking catalyst.

7. Process according to claim 6, wherein the regenerated cracking catalyst is recycled to the pyrolysis treatment of step a).

8. Process according to any one of claims 1 to 7, wherein the feed stream comprises biomass selected from the group consisting of agricultural waste, plants, wood and combinations thereof.

9. Process according to any one of claims 1 to 7, wherein the feed stream comprises biomass selected from the group consisting of glucose, maltose, starch, cellobiose, cellulose, hemi-cellulose, other polysaccharides, lignin, sugar cane bagasse, lignocellulosic materials, food waste, animal waste, manure and corn stover.

10. Process according to any one of claims 1 to 9, wherein the conversion treatment in step c) is carried out at a temperature in the range of 300 to 1000°C and a pressure in the range of 1 to 4 bar.

11. Process according to any one of claims 1 to 10, wherein the second, aromatization catalyst is a zeolitic catalyst, suitably selected from aluminosilicates, SAPOs, silicalites and combinations thereof.

12. Process according to any one of claims 1 to 11, wherein the second, aromatization catalyst is acidic.

13. Process according to claim 12, wherein the second, aromatization catalyst is made acidic by ion exchange with ammonium salts and subsequent calcination.

14. Process according to any one of claims 1 to 13, wherein the second, aromatization catalyst has been selected from the group consisting of ZSM-5, ZSM-11, ZSM-35, ZSM-23, ferrierite, zeolite beta, zeolite Y, zeolite X, mordenite, zeolite A, IM-5, SSZ-20, SSZ-55, MCM-22, TNU-9 and combinations thereof.

15. Process according to any one of claims 1 to 14, wherein the second, aromatization catalyst comprises an amorphous binder in addition to a zeolite.

16. Process according to claim 15, wherein the amorphous binder has been selected from inorganic refractory oxides, in particular alumina, silica, silica-alumina, titania, zirconia or mixtures thereof, preferably silica-alumina.

17. Process according to claim 16, wherein the amount of amorphous binder in the second, aromatization catalyst is in the range of 0 to 80 %wt, based on the weight of the zeolite and the amorphous binder.

18. Process according to any one of claims 1 to 17, wherein the conversion treatment is carried out in a fixed bed, a moving bed or a fluidized bed.

19. Process according to any one of claims 1 to 18, wherein the conversion product is subjected to fractionation, yielding aromatic compounds as separate fraction or fractions and a residue.

20. Process according to claim 19 wherein the residue is combusted to yield energy.

21. Process according to claim 19 or 20, wherein the conversion product is subjected to fractionation yielding an olefin fraction.

22. Process according to claim 21, wherein at least part of the olefins fraction is recycled to the conversion treatment or to the pyrolysis treatment or to both.

23. Process according to any one of claims 1 to 18, wherein the aromatic compounds are recovered from the conversion product, which process comprises contacting the conversion product with a liquid hydrocarbon to obtain a hydrocarbon phase containing aromatic compounds, and an oxygen-containing compound phase, and separating the hydrocarbon phase from the oxygen-containing compound phase.

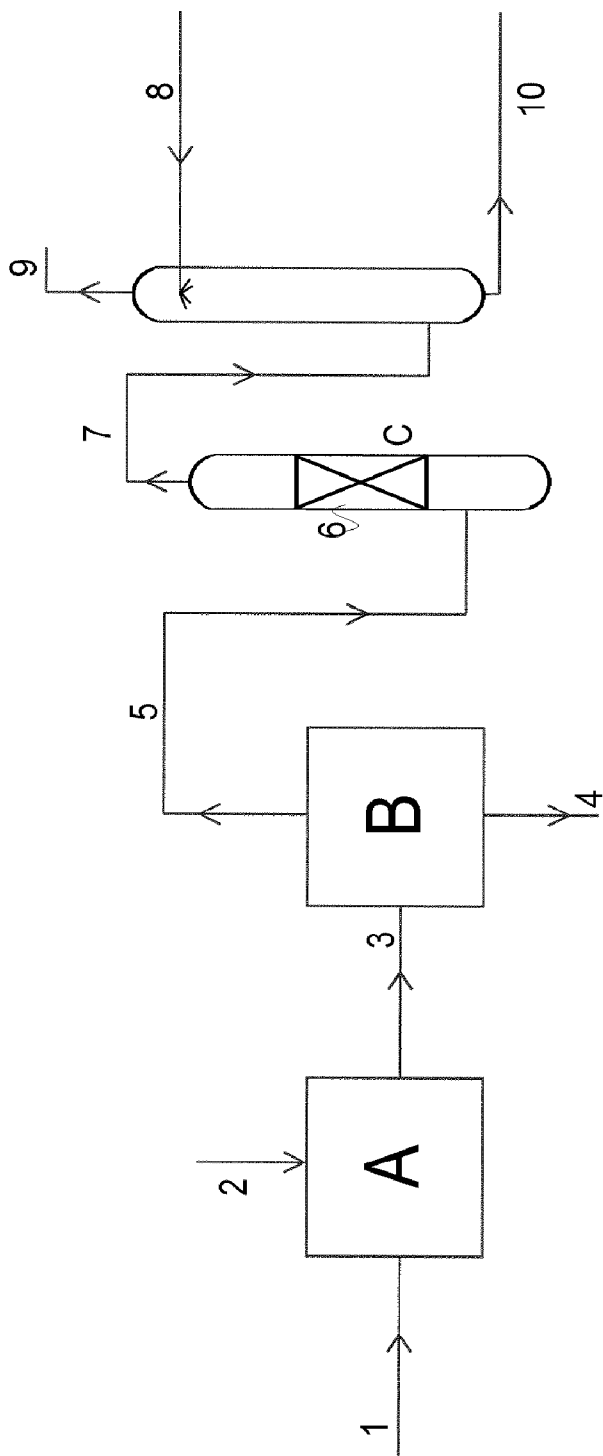


Fig. 1.

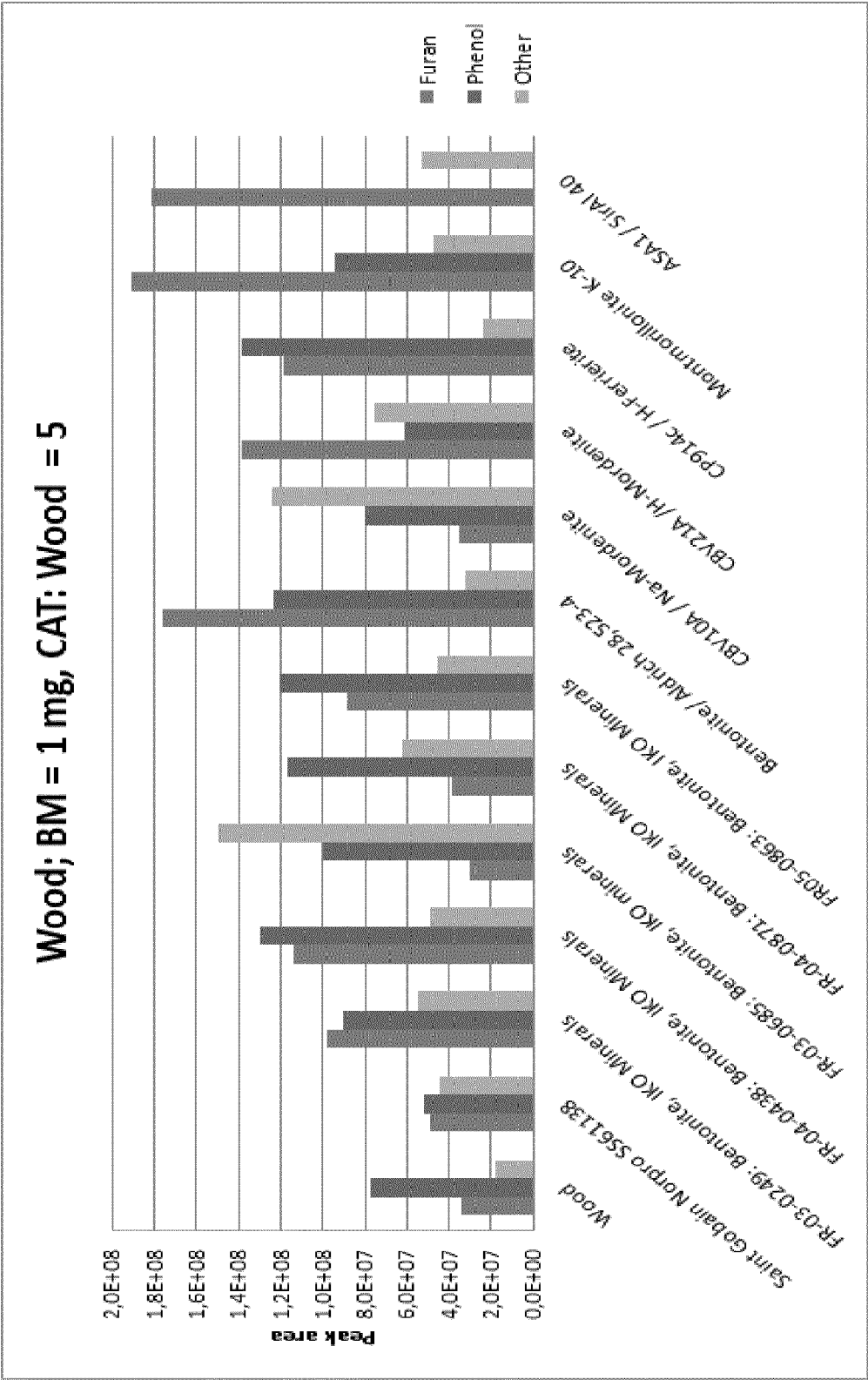


Fig 2.

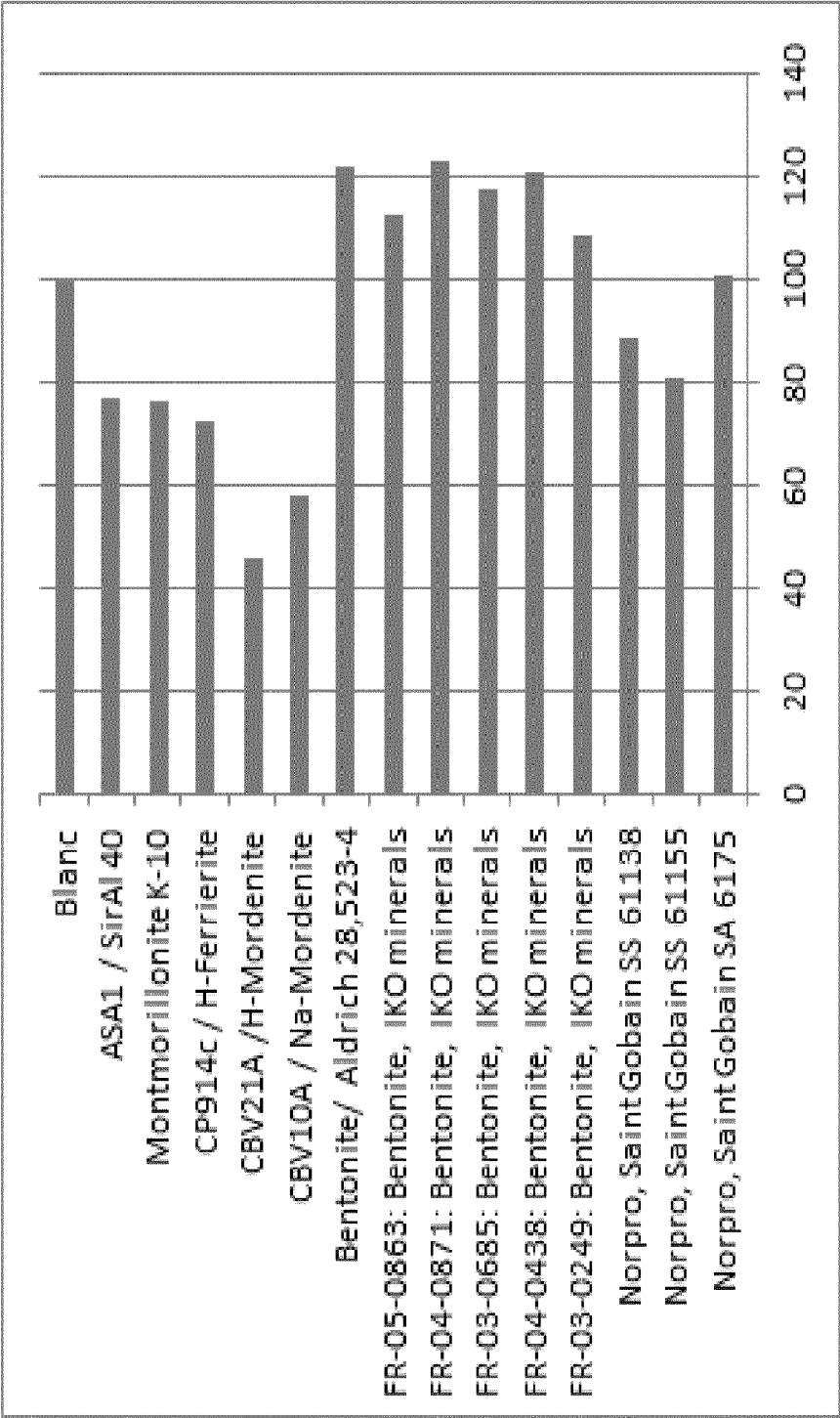


Fig 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2014/050653

A. CLASSIFICATION OF SUBJECT MATTER INV. C10B53/02 C10B57/06 C10G1/08 C10G3/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10B C10G		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, COMPENDEX, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/283601 A1 (DITSCH ANDRE [US]) 24 November 2011 (2011-11-24)	1-22
Y	claims 1-34 figures 1,2 paragraphs [0021], [0022], [0041], [0042]	1,3,23

X	James Diebold ET AL: "Biomass to Gasoline" In: "Pyrolysis Oils from Biomass", 30 September 1988 (1988-09-30), American Chemical Society, Washington, DC, XP055114410, ISBN: 978-0-84-121228-2 vol. 376, pages 264-276, DOI: 10.1021/bk-1988-0376.ch023,	2,4-22
Y	Experimental Conclusions table II	1,3,23

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<div style="display: flex; justify-content: space-between;"> ☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex. </div>		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">12 January 2015</div>	Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">19/01/2015</div>	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <div style="text-align: center; font-weight: bold;">Zuurdeeg, Boudewijn</div>	

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2014/050653

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>XIANGYU LI ET AL: "Improving the aromatic production in catalytic fast pyrolysis of cellulose by co-feeding low-density polyethylene", APPLIED CATALYSIS A: GENERAL, vol. 455, 14 February 2013 (2013-02-14), pages 114-121, XP055114413, ISSN: 0926-860X, DOI: 10.1016/j.apcata.2013.01.038 figure 4 table 2 abstract</p>	1
X,P	<p>-----</p> <p>André Heeres ET AL: "BioBTX aims for production of aromatics by catalytic pyrolysis of biomass and plastic waste", PyNe Issue 34, 1 January 2014 (2014-01-01), pages 13-14, XP055159953, Retrieved from the Internet: URL:http://www.pyne.co.uk/Resources/user/P yNe%20Newsletter%20Issue%2034%20January%20 14%20PUBLISHED.pdf [retrieved on 2015-01-05] page 14</p>	1,2,4-22
Y,P	<p>-----</p> <p>OFEI DAKU MANTE ET AL: "Catalytic conversion of biomass to bio-synchrude oil", BIOMASS CONVERSION AND BIOREFINERY, vol. 1, no. 4, 20 August 2011 (2011-08-20) , pages 203-215, XP055160010, ISSN: 2190-6815, DOI: 10.1007/s13399-011-0020-4</p>	23
X	<p>-----</p> <p>figures 1,6,7 2.3 Catalytic pyrolysis 2.4 Bio-oil analysis 3.5 Chemical composition of bio-synchrude oils 4 Conclusion</p>	1,4-22
Y	<p>-----</p> <p>SOLAK AGNIESZKA ET AL: "The effect of clay catalyst on the chemical composition of bio-oil obtained by co-pyrolysis of cellulose and polyethylene", WASTE MANAGEMENT, ELSEVIER, NEW YORK, NY, US, vol. 34, no. 2, 16 November 2013 (2013-11-16), pages 504-512, XP028810259, ISSN: 0956-053X, DOI: 10.1016/J.WASMAN.2013.10.036 2.1 Samples 2.2 Pyrolysis figures 1,3</p>	23
Y,P	<p>-----</p> <p>-----</p> <p>-/--</p>	1,3

INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2014/050653

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	<p>LIU HAIBO ET AL: "Effect of palygorskite clay on pyrolysis of rape straw: An in situ catalysis study", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS, NEW YORK, NY, US, vol. 417, 22 November 2013 (2013-11-22), pages 264-269, XP028671501, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2013.11.041</p> <p>2. Experimental</p> <p>3. Results and discussion</p> <p>4. Conclusions</p> <p>-----</p>	1
Y	<p>WO 2011/138357 A1 (BASF SE [DE]; PROCHAZKA ROMAN [DE]; BITTERLICH STEFAN [DE]; MACHHAMMER) 10 November 2011 (2011-11-10) page 18, line 7 - page 20, line 13 claims 1,14,15</p> <p>-----</p>	23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/NL2014/050653

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2011283601	A1	24-11-2011	NONE	

WO 2011138357	A1	10-11-2011	NONE	
