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Biomass based energy intermediates boosting biofuel production

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Deliverable

Report

DELIVERABLE 5.4: APPLICABILITY OF CATALYTIC PYROLYSIS LIQUID (CPL) FOR DIFFERENT UPGRADING METHODS INCLUDING SELECTION OF THE METHOD

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COOPERATION

Publishable Summary

Existing fluid catalytic cracking (FCC) units, hydrotreating (HT) and hydrocracking (HC) units or a possible combination of units are possible entry points for the upgrading of catalytic pyrolysis liquid (CPL) into traffic fuel components in oil refineries. In FCC units, high molecular weight (MW) hydrocarbons are cracked and the MW product profile is reduced. In the HT and HC units, external hydrogen is added to remove heteroatoms such as sulphur and nitrogen (HT) or to shorten carbon chain length (HC).

A range of factors and criteria were used in this assesment as to what process concept and units would be best applicable for CPL upgrading in an oil refinery and these were: (1) results of Neste Oil experimental work on upgrading; (2) known similarities in composition between thermal pyrolysis liquid (TPL) and CPL; (3) technical constraints and requirements for high availability in existing oil refineries, (4) current legislative framework; (5) the amount of MW reduction that would be required in order to produce the desired gasoline / diesel components and (6) lessons learned from earlier studies on upgrading.

Based on these considerations, a preliminary upgrading concept proposal is that the introduction of CPL into an oil refinery would be in dedicated hydrotreater(s) that are integrated into the refinery infrastructure. Due to the unstable nature of CPL, this would include an initial mild hydrotreating step (HT1) followed by a second step (HT2) using more severe conditions. The final conditions as well as the catalyst used for these steps has not yet been determined.

Contents

1 INTRODUCTION

Conversion of wood and straw biomass into intermediate liquid energy carriers by a thermal pyrolysis process (TPP) or a catalytic pyrolysis process (CPP) with further upgrading into traffic fuels has been receiving considerable attention in recent years as the search for cost competitive biofuels from non-food biomass intensifies. Although considerable work has been done in this area, scale up and commercial production is still in the early stage. The front runner in commercialization is KiOR in the United States which is operating a 35 000 tonne/a plant.

Within the BioBoost project, Neste Oil is investigating possible pathways for introducing catalytic pyrolysis liquids (CPL) into an oil refinery. The two main routes being considered are the hydrotreating route where hydrogen is used to remove oxygen as water and this is called hydrodeoxygenation (HDO). The HDO can be either a hydrotreating (HT1) unit or a hydrocracker (HT2). The HT2 uses higher temperatures and hydrogen pressures than the HT1. Another possible entry point of the refinery is the fluid catalytic route (FCC) unit where the CPL may be mixed with existing feeds and co-fed into the FDD. Both of these routes have been studied extensively over the years on mainly thermal pyrolytic liquids (TPL) (Annex 1) by a large number of investigators and programmes such as the EU BioCoup project, studies conducted by Veba Oil on Ensyn fast pyrolysis oils together with CERTH, as well as separate studies by CERTH, early work by Ed Soltes on Georgian Tech tars, work done by Doug Elliot at PNNL, the UOP / Ensyn JV company Envergent, as well as many others.

In our concept analysis we have combined the learnings from these groups together with reliability and availability of refinery unit aspects and also legislative considerations on mandates for biofuels in the traffic sector and the results of our experimental work to date.

The routes being suggested in this report should be considered as preliminary and may be modified as our work proceeds.

2 LESSONS LEARNED FROM UPGRADING STUDIES

Most of the current literature on upgrading of pyrolysis liquids concerns studies on TPL. This is because until fairly recently there have not been many groups that could produce CPLs. Some of the lessons learned on TPL upgrading can be used in devising concepts for the upgrading of CPL while at the same time it should be noted that some of the conclusions on TPL upgrading do not apply to that of CPL upgrading. These will be briefly looked at here.

In the case of TPP processes, it is well known that due to the fact that TPL has very high oxygen content removal of oxygen by hydrodeoxygenation (HDO) leads to high hydrogen consumption. This increases the processing costs and lowers the environmental performance of the products as hydrogen is normally produced from natural gas and this is a major source of carbon dioxide emissions. Replacing this with biomass derived hydrogen increases costs even further. In addition, TPLs contain significant amounts of high molecular weight lignin which leads to high levels of coke formation. Based on these findings with the HDO route, interest then has begun to shift to the fluid catalytic cracking (FCC) route. Here hydrogen required for bond saturation or in oxygen removal as water, is obtained from the feed itself. This leads to increased amounts of coke. Another feature of the FCC process is, it is a cracking process, where the average molecular weight (MW) of the feed is reduced.

The FCC process was extensively investigated for example in the EU BIOCOUP project on upgrading ? TPL. To decrease coking, a first stabilization step of the TPL by hydrogenation together with addition of a diluent such as vacuum gas oil (VGO) was tested. Co-processing of stabilized TPL in catalytic cracking (FCC) was shown to be a much better alternative than processing the stabilized TPL without dilution. Without dilution lower product yields were obtained due to higher dry gas and coke formation. The product was hydrogen deficient as no hydrogen is added during catalytic cracking.

Co-processing of 20 wt-% hydrodeoxygenated bio-oil in typical FCC feed resulted in a product with similar properties as for the reference FCC case. The suitable amount of HDO-oil to be added was determined by the coking tendency of the mixture (determined with TGA or by the MCRT test). The benefit with co-processing is that the hydrocarbons in the fossil feed act as a source for hydrogen transfer to increase the stability of the system and as a diluent to reduce polymerisation reactions.

But even with these stabilization steps and restricting the overall blending amount of TPL in an FCC to less than 20 % in laboratory scale and 5 % in pilot scale, the results clearly showed that coking increased more than for normal mineral oil processing. This caused reactor plugging and catalyst deactivation (= coking) which was initiated by the tendency of TPL to polymerize even at mild conditions.

In general, the challenge for bio-oil upgrading is the competition between thermal and catalytic reactions, where the thermal reactions are commonly much faster than the catalytic ones. Thermal reactions are the main reason for (re)polymerisation and coke formation. Carbon deposition on catalysts is more extensive in catalytic cracking compared to HDO. The removal of oxygen from phenolic compounds is another challenge. In HDO it means more severe conditions to obtain higher degree of deoxygenation and at the same time it results in lower oil yields due to increased water and gas formation. The conversion of phenolic compounds in catalytic cracking is known to be even more demanding.

This FCC route could be feasible in the future if the quality of CPL is sufficiently improved but there will remain similar challenges for this route as CPL still contains high MW aromatic lignin fragments.

Based on a broad look at the available literature and the many similarities between TPL and CPL, we can expect that similar issues will be faced in upgrading of CPL to HCs.

3 CPL UPGRADING OPTIONS

3.1 ROUTES

In this work, two main catalytic routes have been considered for the upgrading of CPL: hydrodeoxygenation (HDO) and fluid catalytic cracking (FCC). The HDO route may include a mild, initial hydrotreating (HT1) step in order to stabilize the CPL feed followed by a more severe hydrotreating (HT2) step where temperatures and or hydrogen pressures are raised but still less than in normal refinery hydrocrackers.

3.2 HDO Features

- CPL requires a separate stabilization step HT1 (mild temperatures, 150 – 250 °C have been suggested) comparable to the one proposed for thermal pyrolysis oils in order to remove the most reactive centers and avoid coking and polymerization
- this will be follwed by a HT2 hydrodeoxygenation (and mild hydrocracking) step using higher temperatures (300 -350 °C) but with similar hydrogen pressures
- using similar hydrogen pressures would allow the HT1 and HT2 steps to be in the same reactor
- hydrotreating steps are exothermic so heat removal and control will be an important feature of the process units

- the reaction conditions given are currently under assessment and will depend on the catalyst used, the composition of CPL and the slate of products that are desired

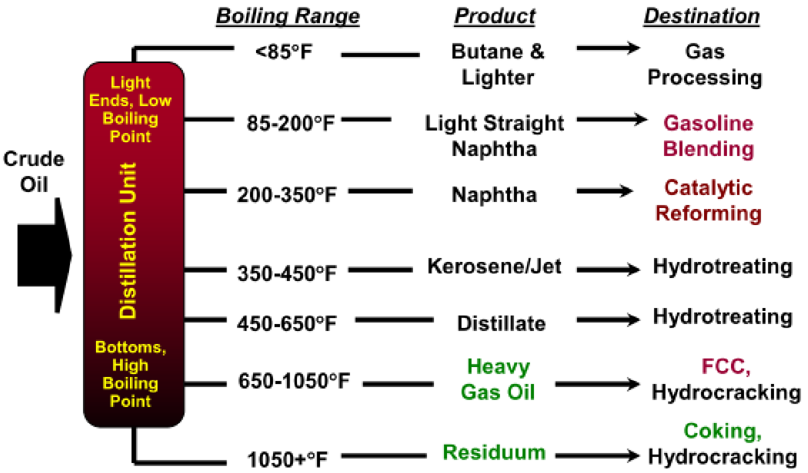
3.3 FCC Features

- in the FCC process extensive cracking occurs but CPL components are already mainly in the gasoline and jet fuel range and extensive cracking is not needed
- hydrogen is not added in the FCC process and hydrogen transfer occurs between molecules; CPL has been produced in an FCC like process it is already hydrogen deficient and so this would lead to further coking
- CPL contains lignin derived aromatic fragments with low crackability, but high coke-forming tendency; side chains connected to aromatic rings readily undergo cracking reactions forming an olefin, leaving the aromatic ring intact
- in co-processing it is probable that a greater part of CPL will form coke - due the oxygenates and aromatics present - compared to fossil FCC feeds

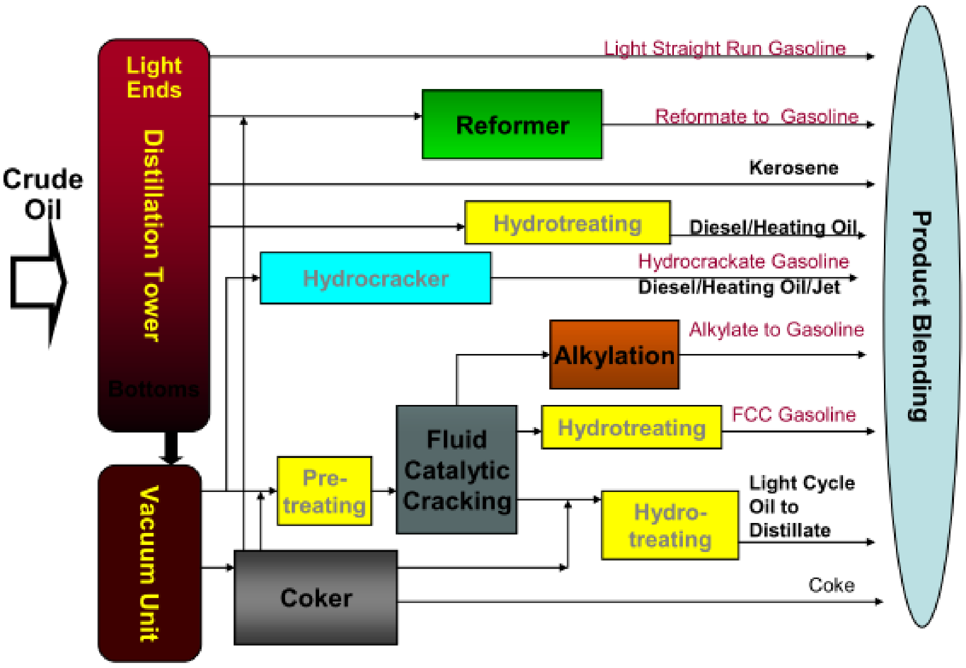
4 OIL REFINERIES

4.1 REFINERY UNITS

FONTTI ON MUUTTUNUT Oil refineries are comprised of a large number of individual units. In general, the more units included in the refinery, the more products that are formed, the more complex the refinery becomes. The main refinery units are presented below together with a short description of the Neste Oil Porvoo refinery.



Temperatures in the individual units are influenced by the type of feed and the catalyst that are used and vary somewhat.



(teksti oli jäänyt kuvan alle…) In addition to the refinery units themselves, there are processes for the production of steam and power as well as hydrogen and water treatments etc.. There are also storage facilities for crude oil and tank farms for finished products. Depending on the location of the refinery the crude feeds and products can be transported by pipeline, ships, rail as well as road.

4.2 NESTE OIL PORVOO REFINERY

The Porvoo refinery is focused on the production of premium-quality, low-emission traffic fuels. It has four production lines and more than 40 process units producing more than 150 products and product components. The refinery came on stream in 1965 and is composed of the following units:

Porvoo refinery, nameplate capacities	1000 t/a	t/h
Atmospheric Crude Distillation	10200	1164
Vacuum Distillation	4070	465
Hydrocracking	1150	131
Visbreaking	1480	169
Fluid Catalytic Cracking	2230	255
Gasoline Reforming	1 875	214
Distillate Aromatics Saturation	850	97
VGO Desulfurization	2970	339
Alkylation	315	36
ETBE	123	14

EHVI Unit	350	40
NExBTL 1 & 2 Units	525	60
Residue Hydrocracking Unit	3060	349

5 UPGRADING ASPECTS UNDER CONSIDERATION

5.1 TECHNICAL ASPECTS

i. CPL Acidity. The acidity of CPL is important as most materials in refinery storage tanks are carbon steel which could corrode if CPL is acidic. There are some mild acids and water retained in the CPL phase which could corrode normal storage tanks depending on the conditions of storage. The risk of corrosion at lower temperatures must be assessed.

ii. Catalyst poisons / contaminants. All catalysts are not sensitive to all metals. A specification of the minimum CPL quality has been given earlier for normal refinery feeds. This specification will be reviewed with the analysis of metals content of a typical CPL to identify any areas of concern. The effects on catalyst lifetime caused by the introduction of any new metals even at low concentrations are determined by conducting catalyst life tests (depending on the metal in question). In this project the risk will be evaluated based on analyses.

iii. Stability. In order to pump the CPL into the refinery feed lines, the viscosity must be sufficiently low. This may require heated tanks. In addition, prior to feeding into the refinery units, the CPL must be heated up to operating temperatures. This is normally done in heat exchangers. This requires that CPL does not react or form deposits on the heat transfer surfaces. Heat transfer surfaces have been designed according to the properties of mineral oils and surface temperatures can be quite high compared to the liquid temperature itself. Depending on the miscibility with refinery streams, this could be prevented by storing as a mixed fuel.

iv. Miscibility. In order for the co-feed concept to work, the CPL must be miscible with the normal feeds such as vacuum gas oil which is the normal feed into the FCC. But since CPL contains water, some organic acids along with other oxygenated compounds the mixing could prove problematic. Mixing of CPL with VGO at appropriate temperatures with a follow up of short term and long term stability will be done.

v. Coke formation. Coke is normally formed in the pores of the FCC catalyst during normal operations which is then removed by combustion to regenerate the catalyst. The FCC reactor is in heat balance when using normal mineral oil feeds and the energy required to drive the reaction is produced from coke combustion. If excess coke is formed or if the coke that is formed is more stable than normal coke then this would have a negative influence on the conversion (yield) of the unit and the need for catalyst make up. This may only be resolved by running long term tests on representative samples.

vi. Hydrogen pressure requirements. When using existing hydrocracking or hydrotreating units, there is a certain hydrogen pressure under which the units operate. Hydrotreating is used to remove sulphur from mineral oils and also called hydrodesulphurization. Normal hydrogen pressures are typically 50 to 60 bar. In the experimental section of our work, it has been shown that pressures up to 150 bar will be required in order to remove oxygen.

5.2 ECONOMIC ASPECTS

i Increased Storage Costs: If the acidity of CPL is too strong for mild carb steels normally used in storage tanks, it will be necessary to either apply a protective coating to the existing materials or to use more expensive steels. Also depending on the stability of CPL, it might be necessary to use more expensive solutions for heating of the storage tanks.

ii Pre-treatment Costs. Depending on the thermal stability CPL at the temperature of the unit in question or at the temperature of the heat exchangers used to bring the CPL up to input feed temperatures, it might be necessary to install a pre-treatment unit or stabilization unit prior to the HDO unit itself. Our first results from our experiments and our understanding of the thermal reactivity of the compounds found within CPL indicate that such a stabilization unit would be needed.

ii. Heat transfer surfaces. In order to heat mineral oil feeds to the required temperatures, they are passed through heat exchangers or through heating tubes in ovens. If the CPL has a tendency to form deposits, then it might be necessary to introduce separate heat exchangers which have less intense heating or are coated to avoid deposits. This risk could be minimized by premixing with a refinery feed. This will be looked at during the miscibility tests.

iii. Washing. In the production of CPL two phases are formed. The first being an aqueous phase and the other being the organic phase. The organic phase is not completely non-polar due to the presence of oxygen. This organic phase contains both water and some organic acids. This might require a further washing to remove these acids.

iii. Hydrogen costs. In refineries hydrogen is normally produced in a steam methane reformer (SMR). The feed is primarily methane but also refinery gases may be used. A typical hydrogen cost is about 1.5 €/kg. Costs for hydrogen are highly dependent on the cost of natural gas as well as the overall efficiency of the process. The experiments being conducted by Neste Oil are investigating the reaction conditions i.e. hydrogen pressure, reaction temperatures and catalyst amounts necessary to remove oxygen. From these experiments we will estimate the hydrogen consumption.

iv. Effect of Process conditions on yields. In order to produce drop in hydrocarbon fuels from CPL, it will be necessary to remove all of the oxygen from the CPL. In order to remove all of the oxygen it may be necessary to raise hydrogen pressures and reaction temperatures (severity of the process) to remove the oxygen from the most stable compounds. This could cause an increased production of light gases that do not enter the transportation fuel pool. This combination of high hydrogen consumption and reduced yields of biofuels would have a negative effect on overall economics.

v. Catalyst Consumption. Increased catalyst consumption (in FCC reactors) or shortened catalyst lifetime (in the hydrotreater or hydrocrackers) caused by the introduction of CPL into the refinery units could have a negative impact on the host process in addition to the catalyst costs themselves. If this occurs then the costs due to lowered production in existing units can be quite high. Some rough estimates for increased catalyst consumption / decreased catalyst lifetime will be performed.

5.3 LEGISLATIVE ASPECTS

The European Union directive on biofuels, the so called RED directive, sets in place a framework by which member states must over time increase their use of biofuels as a portion of traffic fuels used. There is no such mandate for heating fuels or chemicals consumption. For this reason it is important to maximize the yield of upgraded CPL products that are used as diesel or gasoline blend stocks. Some refinery processes produce a slate of products that are used in other applications. A dedicated process allows the maximum capture in the traffic fuel pool.

6 LESSONS LEARNED FROM NESTE OIL EXPERIMENTAL WORK TO DATE

6.1 CPL PROPERTIES AND COMPOSITON

The catalytic pyrolysis process produces a two phase product, an upper aqueous phase and a lower organic phase which are separated at the production plant. The bottom phase product was received by Neste Oil and the physical properties and chemical characterization of the organic phase were analysed and have been reported separately. The samples showed further phase separation upon standing into an upper phase and lower phase with time. The lower and upper phases were analysed. The upper aqueous phase was highly acidic and will be removed at the catalytic pyrolysis production plant.
The properties that affect the shipping, storage and upgrading of the bottom organic phase are the acidity, flash point, water and oxygen content.

6.2 TEST RUNS RESULTS

6.2.1 Experimental Set-Up

The experiments to date have been conducted in a PARR stirred batch reactor where the catalyst is placed in a wire mesh basket. The first experiments have been conducted without catalyst and with nitrogen to drive off remaining acids and water. HDO catalyst tests at a number of pressures and temperatures have been run. A typical refinery hydrodesulfurization catalyst was used.

Prior to each experiment, the reactor is filled with about 50 grams of CPL, pressurized and left for 10-15 hours to ensure that the reactor is gas tight.

6.2.2 Heating Under Nitrogen

In this heating experiment, the goal was to drive off the water and the acids using an inert gas such as nitrogen. The sample was heated in the reactor over a period of 4-5 hours. Samples were trapped. Samples contained both the acids and some of the light hydrocarbons.

It was found that significant amounts of light hydrocarbons were driven off together with the water and light acids.

6.2.3 HT1 and HT2 of CPL

After determining suitable conditions for reactor operations, tests were started on HDO and stabilization. Temperatues were held in the 240 – 260 ^{o}C range for a short period before raising temperatures to around 320 ^{o}C. Hydrogen pressures were increased in each experiments from around 80 bar final pressure in the first set of experiments to 145 bar in the current set of experiments. Oxygen content in the product has reduced progressively over the course of the experiments but is still present in various compounds as given below.

6.2.4 GC-MS of CPL Products

The main components identified by GC-MS in the liquid oil phase of hydrotreated CPL are shown in Table 1 and some examples of the structures are shown in Figure 1. These compounds were also present in the catalytic pyrolysis oil. Due to experimental set up, the majority of the lighter compounds were entrained in the exit flow stream of the hydrogen gas and are not included with these analyses.

Table 1: Main groups of compounds in the oil product obtained in hydrotreatment of catalytic pyrolysis oil (test 4)

Compound group	Alkyl ligand(s)	Total carbon number
Alkylbenzenes	C1 -C7	C7 - C13
Indanes	None or C1 - C3	C10 - C12
Naphthalenes	None or C1 - C3	C11 - C13
Phenols	None or C1 - C4	C6 - C10
Indanols	None or C1	C9 - C10
Benzofurans	None or C1 - C2	C8 - C10

Compared to the catalytic pyrolysis oil used as feed, the composition was less complex after hydrotreatment. In the reaction conditions used, both hydrogenation and hydrodeoxygenation reactions took place: aliphatic C=C double bonds were hydrogenated (including methylene-, vinyl- and allyl-groups attached to aromatic rings) and keto-, formyl-, hydroxyl- and alkoxy-groups were hydrodeoxygenated. These reactions were seen as diminished amounts of styrenes, indenes, aliphatic O-compounds (especially cycloketones), benzenediols, indenols, naphthols and aromatic O-compounds with methoxy-groups (see examples of components in Figure 2).

The reaction conditions used were not yet severe enough to give complete oxygen removal, leaving phenolic compounds and benzofurans in the product. The reactivity of oxygenated groups followed the order proposed in literature. No aliphatic hydrocarbons were observed in the oil phase.

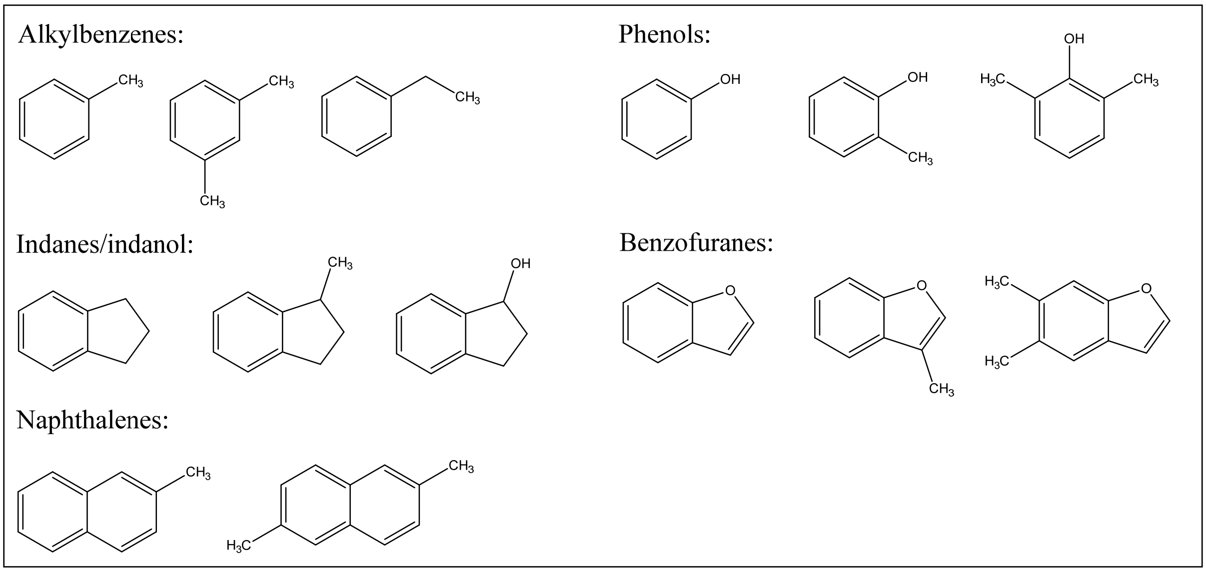


Figure 1: Representatives of components in oil phase of hydrotreated catalytic pyrolysis oil (in test 4)

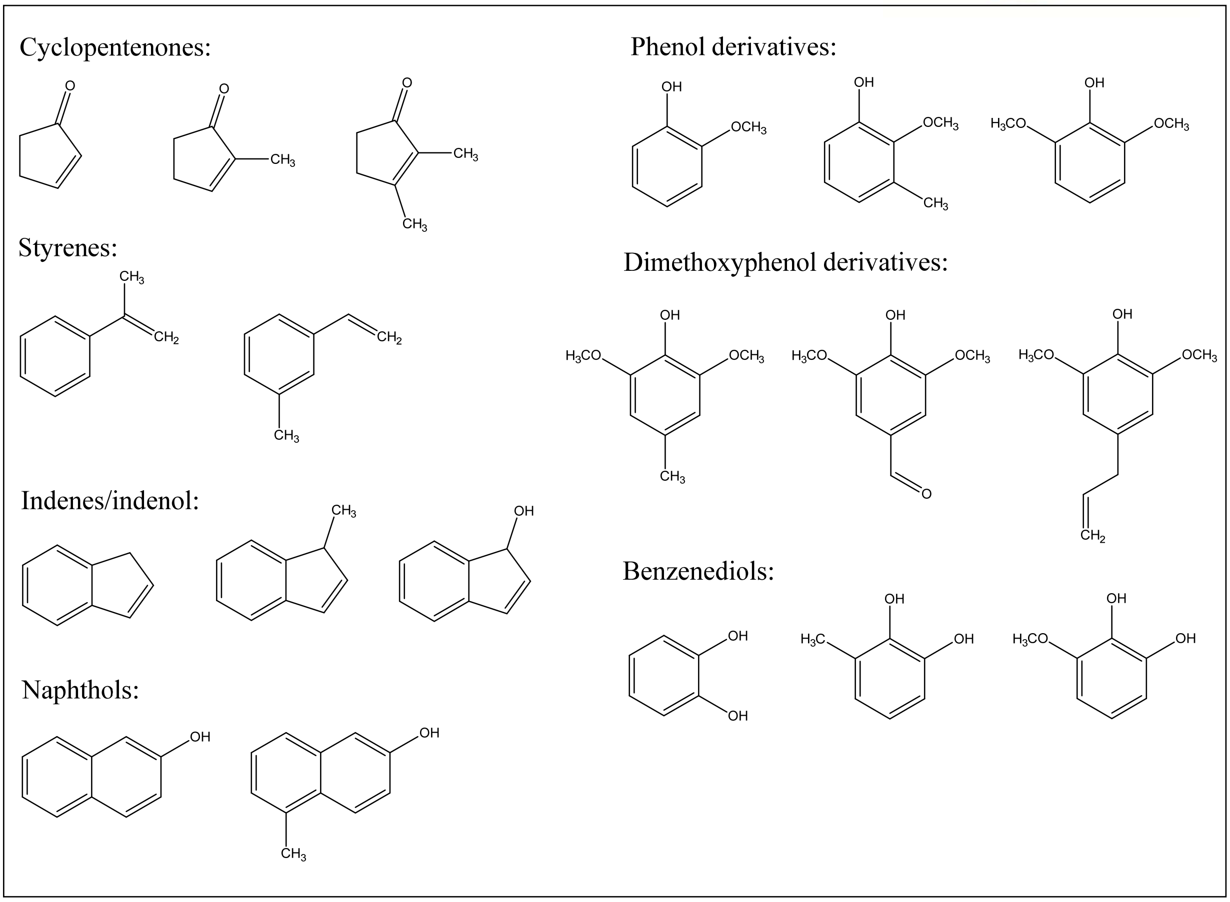


Figure 2: Representatives of components with functional groups being hydrogenated and hydrodeoxygenated during hydrotreatment.

7 SELECTION OF CONCEPT

7.1 CATALYSTS

Catalysts utilized for HDO have commonly been either conventional hydrotreating catalysts (sulphided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$) or noble metal catalysts. Ru/C has been proposed as a promising noble metal catalyst. Aluminium oxide suffers from phase transition to boemite ($AlO(OH)$) in the presence of water making it less attractive as support in HDO processing. Catalyst deactivation during HDO is still an issue to be resolved. Regardless of the type of catalyst (and HDO mechanism) the main cause of deactivation is coke deposition.

7.2 CONCEPT

A two-stage process is suggested and is further detailed in Annex 2. It begins with a stabilization step to protect / eliminate the reactive components and prevent coke formation. Temperatures in the range of 150-250 ^{o}C. In the subsequent deep HDO or HT2 step at elevated temperatures (320-370 ^{o}C) a very high degree of deoxygenation (>99 %) is achieved. Both steps were carried out at high pressure (150-200 bar) in order to ensure the solubility of hydrogen in the CPL. The temperatures and pressures can be adjusted to permit the extraction of desired compounds. Phenolics are among the most difficult compounds to convert and may be removed prior to or after HT2. To limit hydrogen consumption, saturation of aromatics is proposed to be avoided. The conditions that would be normally used are under investigation.