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Biomass based energy intermediates boosting biofuel production

This project has received funding from the European Union’s Seventh Programme for research, technological development and demonstration under grant agreement No 282873

Deliverable

Process concept on upgrading and utilization of catalytic pyrolysis oil at NESTE Oil refineries

Workpackage:	WP5
Deliverable N^{o}:	D5.10
Due date of deliverable:	01/09/14
Actual date of delivery:	15/01/15
Version:	Final
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Dissemination level:	PU-Public

Contents

Summary

Concepts for upgrading of catalytic pyrolysis oil (CP oil) into traffic fuel components in a Neste Oil refinery were studied.

The following criteria were used for selection of the concept: (1) results and experiences of Neste Oil experimental work on CP oil upgrading using samples provided by BioBoost partner CERTH; (2) composition and properties of CP oils (3) lessons learned from scientific literature (4) recent developments and progress of catalytic pyrolysis process developers; (5) the types of challenges and solutions in the upgrading of thermal pyrolysis oil (TP oil) while taking into account compositional similarities and differences between and CP oil and TP oil; (6) technical risks and constraints when introducing new feeds into existing oil refinery units, (7) current legislative framework concerning support mechanisms and mandates for renewable traffic fuels

Based on an analysis of a combination of the above factors, it was concluded that the most applicable process concept for the upgrading of CP oils in conventional oil refineries is dedicated hyrotreaters integrated into the refinery infrastructure. This type of integration poses the least risk to existing refinery units while reducing investment costs over a standalone unit. This concept also allows the isolation of the full biofuel production.

Neste Oil experimental work explored this concept in a series of experiments and our preliminary results have indicated that this concept would be feasible in the future when the concept is further developed.

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 commercialization is still in the early stage. A number of companies are pursuing this route such as KiOR, Criterion catalysts and RTI International all from the United States. A major reason for this rather slow progress is that the conversion of biomass (lignocellulosic) into traffic fuels is in general more complex than for first generation technologies and the processes require more steps than first generation technologies. In addition, the catalysts for these processes much be developed and tested. These additional process steps and complexity lead to higher investment costs especially for the first plants. And although this is compensated for by lower feedstock costs, the yields from these processes are lower than for ethanol from sugar or biodiesel from vegetable oils and so fairly large amounts of biomass feedstock is required in the commercial plants.

With respect to the TPP processes such as that of BioBoost partner KIT, Ensyn of Canada, BTG of the Netherlands, Fortum of Finland as well as others, the upgrading of TP oils into traffic fuels could be accomplished by a number of routes such as gasification to synthesis gas and catalytic conversion or hydrotreating and / or catalytic cracking in an oil refinery. Since the TPP produces an intermediate product by thermally cracking biomass producing liquids, which depending on the exact process configuations, contain 20-30 wt% water, large macromolecules from the lignin and also light organic acids leading to an acidic product. Oxygen is not rejected to any significant degree and so the product has a high oxygen content of 45 - 50 wt%. This combination of high oxygen content, high water content, high acidity and unstable nature of the product leads to high costs in upgrading in oil refineries. For upgrading by hydrotreating, large amounts of hydrogen is required and in the studies to date it has proven very difficult to find suitable catalysts and avoid high coking and low product yields. Other cost factors are more expensive materials in reactors, storage tanks, feed lines, pumps and heat exchange surfaces. In recent years and in order to overcome the high hydrogen consumption required in the upgrading, a catalytic cracking route has been suggested and is being developed. In this route, oxygen is removed as both carbon dioxide and water. Hydrogen required for these reactions is not supplied externally but obtained from the feed molecules. This then leads to a largely aromatic product with increased coke formation. Process developers have then suggested to restrict the amount of bio-oil co-fed into the reactor. The result is then a very small percentage of biofuel in the resultant streams.

In the case of CP oil is has been recognized that due to the large amount of oxygen rejection in the catalytic pyrolysis process (CPP) itself, the hydrogen consumption would be significantly less than from the TPP process. From previous studies by BioBoost partner CERTH as well as other investigators it is known that the oxygen content can be lowered to a 18-22 wt% level which simultaneously improves the stability, reduces the acidity as well as improves the heating value of CP oil as compared to TP oil and this significantly improves the possibility for introducing CP oil into refinery as well as reducing hydrogen consumption.

In the area of catalytic pyrolysis scale-up and commercialization, the first large scale attempt at commercializing this technology by KiOR of the United States which built and operated a 35 000 tonne/a plant. Normal scaling up challenges of a first-of-kind technology were met and the company was not able to achieve the goals set for production volumes. The reluctance of investors to continue to finance this technology has ultimately resulted in bankruptcy of the company. Other companies that are developing similar technologies are RTI International and CRI Criterion Catalysts. A short description of the RTI process can be found here: http://www.rti.org/page.cfm?obj=27B2CDE6-5056-B100-3149261B9B1FBEF3. The intermediate CP oil is upgraded using Haldor Topsoe catalysts. The CRI Criterion IH2 process is briefly described here: http://www.cricatalyst.com/. A key feature of this technology is the addition of hydrogen into the the initial conversion unit which reduces the coking and increases the yield. This technology is now being licensed.

Within the BioBoost project, Neste Oil is investigating possible pathways for introducing catalytic pyrolysis oils (CP oil) into an oil refinery. There are two main routes which have been considered for the upgrading. The first route is the hydrotreating route where hydrogen is used to remove oxygen as water which is called hydrodeoxygenation (HDO). The HDO route may further be divided into a hydrotreating (HT) route or a hydrocracker (HCk). The main difference between these routes is the severity of the process where the HCk route uses higher temperatures and hydrogen pressures than the HT. Due to the much lower amount of oxygen in the intermediate product of CP oil versus TP oil, it is expected that hydrogen consumption will be much less and thus hydrogen cost also much less. An alternative entry point into the refinery is the fluid catalytic route (FCC) unit where the CP oil may be mixed with existing feeds and co-fed into the FCC. Both of these routes have been studied extensively over the years on mainly thermal pyrolytic oils (TP oil) by a 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.

The routes being suggested in this report should however be considered as preliminary and may be modified further as feedback from catalyst testing etc. proceeds.

2 LESSONS LEARNED FROM UPGRADING STUDIES

Most of the current literature on upgrading of pyrolysis oils concerns studies on TP oil. This is due to the fact that until fairly recently there has not been many process developers that could produce CP oils in any quantity. BioBoost partner CERTH has one of the longest experiences in this area. As CP oils are similar to TP oils, some of the lessons learned on TP oil upgrading can be used in devising concepts for the upgrading of CP oil

In the case of TP oil upgrading, it is known that since TP oil has high oxygen content of around 45 weight percent, removal of oxygen by hydrodeoxygenation (HDO) leads to high hydrogen consumption. The cost of hydrogen is highly dependent on the cost of natural gas from which it has been produced and varies from about 1000 Euros to 2500 Euros per tonne hydrogen depending on the cost of natural gas. United States has currently the cheapest natural gas and Asia the most expensive with Europe somewhere in the middle. Renewable hydrogen production costs are roughly double this cost. Therefore processes which consume large amounts of hydrogen will have high processing costs. Another drawback of high hydrogen consumption is due to the high carbon dioxide emissions of hydrogen production. From publically available greenhouse gas calculations concerning hydrogen production it can be found that approximately 10 kg of CO_2 is produced for each kg of hydrogen. To remove the oxygen from TP oil (45 wt% oxygen) using hydrogen, roughly 0.15

kg of hydrogen is consumed per kg of final fuel (44 MJ/kg) thus giving a GHG value of 1500 g CO_2 / 44 MJ = 34 g CO_2 / MJ. Based on the high cost and GHG emissions of this route, interest in TP oil upgrading then has shifted to the fluid catalytic cracking (FCC) route. Here the hydrogen required for bond saturation or in oxygen removal as water, is obtained from the feed itself. The lignin fragments in the TP oil which are highly aromatic lead to increased amounts of coke. As the present FCC units have been designed to handle a very specific amount of coke, it is not possible to significantly increase the amount of coke in current units. Because of this, only relatively small amounts of TP oil may be added to the existing refinery feeds.

The FCC process was extensively investigated for example in the EU BIOCOUP project on upgrading of a stabilized TP oil. To enhance feeding into a refinery, an initial stabilization step of the TP oil by hydrogenation together with addition of a diluent such as vacuum gas oil (VGO) was tested. Co-processing of stabilized TP oil in catalytic cracking (FCC) was shown to be a much better alternative than processing the stabilized TP oil 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.

3 CP OIL UPGRADING OPTIONS

3.1 POSSIBLE UPGRADING ROUTES

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

3.2 HDO Features

- in hydrotreating refinery processes, the feed is introduced into a reactor in the presence of a catalyst under elevated hydrogen pressures and temperatures
- hydrogen is used in refineries to remove heteratoms such as sulphur or nitrogen and also to crack long chain hydrocarbons into smaller molecules; hydrogen pressure is determined by a combination of the type of reaction in question as well as the temperature and catalyst employed
- CP oil requires an initial stabilization step HT (mild temperatures, 150 - 250 ^{o}C have been suggested) under hydrogen pressure comparable to the one proposed for thermal pyrolysis oils in order to neutralize reactive centers and avoid coking and polymerization
- hydrotreating steps are exothermic so heat removal and control will be an important feature of the process units and the reactor must be designed accordingly
- hydrogen consumption is determined by the relative amount of heteroatoms as well as the amount of double bonds

3.3 FCC Features

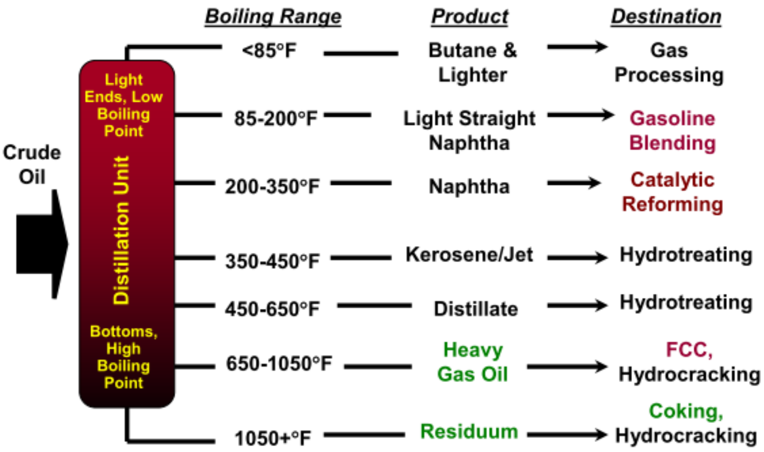
- in the FCC process, feed is preheated feed to 320-420 C and then mixed with hot (about 715 C) catalyst; catalyst is heated in a separate regenerator where reaction coke is combusted, feed and catalyst then enter the riser stand pipe where feed compounds are; operating temperatures in the stand pipe are roughly 500-550 C
- typical feeds are portion of crude oil that has a boiling point > 340 C; the term for the feed is vacuum gas oil (VGO)
- FCC units vary in size depending on the refinery configuration, a typical size is 200-300 t/h (or about 2 million tons/a)
- mainly gasoline range components (naptha) are formed but also light gases as well as compounds with higher boiling points
- hydrogen is not added to the FCC process; hydrogen that is required is obtained from the feed molecules
- aromatic compounds, for example lignin derived fragements from biomass, have inherently low crackability are not normal feeds in FCC due to their high coke-forming tendency

- for a description of a typical FCC reactor and conditions see: http://en.wikipedia.org/wiki/Fluid_catalytic_cracking

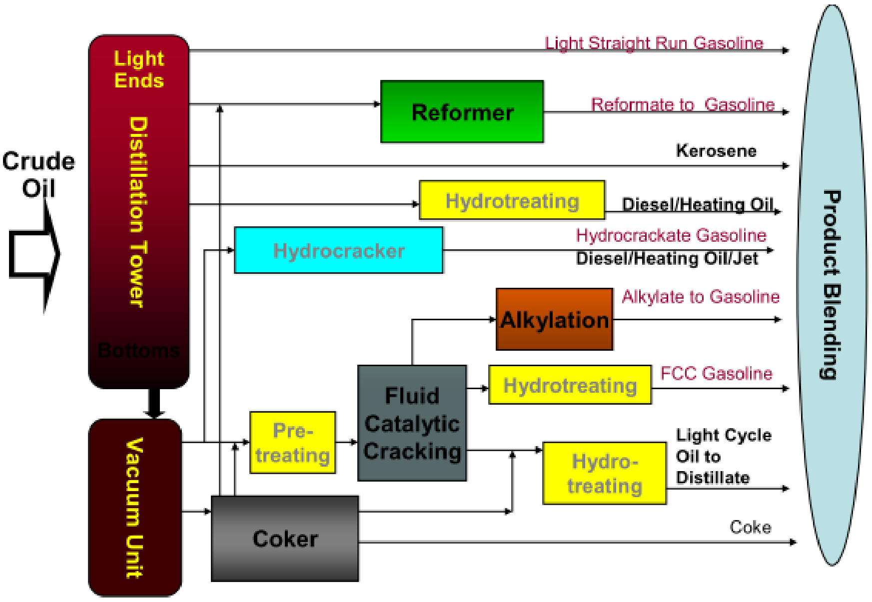
4 OIL REFINERIES

4.1 REFINERY UNITS

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. A list of European refineries is given in Annex II. 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 atalyst that are used and vary to some extent.



In addition to the refinery units, a large number of different types of utilities are required for example the production of steam and power, production of hydrogen, waste water treatment as well as gas cleaning 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 Neste Oil 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 (FCC)	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 CP OIL UPGRADING ISSUES

5.1 TECHNICAL ASPECTS

i. CP oil Acidity. The acidity of CP oil is important as most materials in refinery storage tanks are composed of carbon steel which could corrode if CP oil is acidic. There are some mild acids and water retained in the CP oil 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 CP oil quality has been given earlier for normal refinery feeds. This specification will be reviewed with the analysis of metals content of a typical CP oil 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 CP oil 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 CP oil must be heated up to operating temperatures. This is normally done in heat exchangers. This requires that CP oil 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 CP oil must be miscible with the normal feeds such as vacuum gas oil which is the normal feed into the FCC. But since CP oil contains water, some organic acids along with other oxygenated compounds the mixing could prove problematic. Mixing of CP oil 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 Storage Costs: If the acidity of CP oil 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 CP oil, it might be necessary to use more expensive solutions for heating of the storage tanks.

ii Pre-treatment Costs. Depending on the thermal stability CP oil at the temperature of the unit in question or at the temperature of the heat exchangers used to bring the CP oil 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 CP oil 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 CP oil 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 CP oil 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). See Annex I. The feed is primarily methane but also refinery gases may be used. A typical hydrogen cost is about 1.2-2 €/kg H_2. Costs for hydrogen are highly dependent on the cost of natural gas as well as the overall efficiency of the process. Costs in the United States are lowest.

iv. Effect of Process conditions on yields. In order to produce drop in hydrocarbon fuels from CP oil, it will be necessary to remove all of the oxygen from the CP oil. 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 CP oil 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 CP oil 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

6.1 CP OIL 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 fact that the lower organic phase has a higher density than the upper aquous phase is contrary to what is normally expected and is due to the highly aromatic nature of the organic phase. The CP oil intermeidate product received by Neste Oil was produced by BioBoost partner CERTH. The physical properties and chemical characterization of the organic phase were analysed and have been reported separately. The properties that affect the shipping, storage and upgrading of the bottom organic phase are the acidity, flash point, water and oxygen content.

It is not certain to what extent an improved phase separation would influence the upgrading characteristics of the samples received. The upper aqueous phase was highly acidic and will be removed at the catalytic pyrolysis production plant.

6.2 TEST RUNS RESULTS

The experimental work on CP oils comprised of stabilization and hydrotreatment reactions for the removal of oxygen from the bio-oil in order to produce a hydrocarbon-like product. The results of the Neste Oil experimental work are presented in a separate report. Only the main features and conclusions are reported here.

Preliminary experiments were conducted in a batch reactor to study thermal pretreatments and evaluate suitable hydrotreatment reaction conditions for the CP oil. Screening of reaction conditions were continued using continuous flow in a tubular reactor.

In thermal treatments the maximum temperature was between 95 - 280 °C and the reaction pressure from atmospheric pressure to 125 bar. In two-stage hydrotreatments the stabilization step was carried out at 240 - 260 ^oC and the oxygen removal at 310 - 320 ^oC, both at a pressure of 50-150 bar.

The two-step hydrotreatment was conducted in the tubular reactor by applying a temperature gradient over the reactor tube. In the first test run reaction conditions (H_2 flow rate, liquid feed rate and reaction temperature) were screened.

Based on the experimental results of this study we found that:

1. the oil product yield was approximately 73 wt%
2. the hydrogen consumption (based on dry CP oil feed) was 6 wt%
3. the non-condensable gases (13 wt%) were primarily paraffinic hydrocarbons
4. the CP oil feed requires a stabilization but even then we found catalyst coking
5. under the operation conditions used, we were not able to remove all oxygen

6.3 CP OIL Products

The main components identified by GC-MS in the liquid oil phase of hydrotreated CP oil are shown in the table below. 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: Typical compounds in the heavy oil fraction. (over weighted to the heavier compounds due to the type of recovery system employed).

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

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. This may be partially overcome by choice of reactor and reactor conditions. Catalyst deactivation during HDO remains as one of the important issues to be resolved. Regardless of the type of catalyst (and HDO mechanism) the main cause of deactivation was found to be coke deposition.

7.2 CONCEPT MAIN FEATURES

A two-stage process is suggested and is further described below. Separate (new) hydrotreating reactor or reactors are employed. These are integrated into the infrastructure of the oil refinery using the available utilities such as steam generation, waste water treatment, off gas cleaning and recirculation of hydrogen and hydrogen production. In the experiments performed at Neste Oil catalyst coking occurred after a couple of days of operation. In the subsequent deoxygenation or HDO step, a high degree of deoxygenation (>99 %) was targeted but could not be achieved. Levels of HDO were approximately 90%. This reduces the overall hydrogen consumption but in order to remove all hydrogen, somewhat more severe reaction conditions would be required. Due to the lack of samples and number of runs that could be performed only preliminary conclusions can be drawn from this work.

7.3 CONCEPT DETAILS

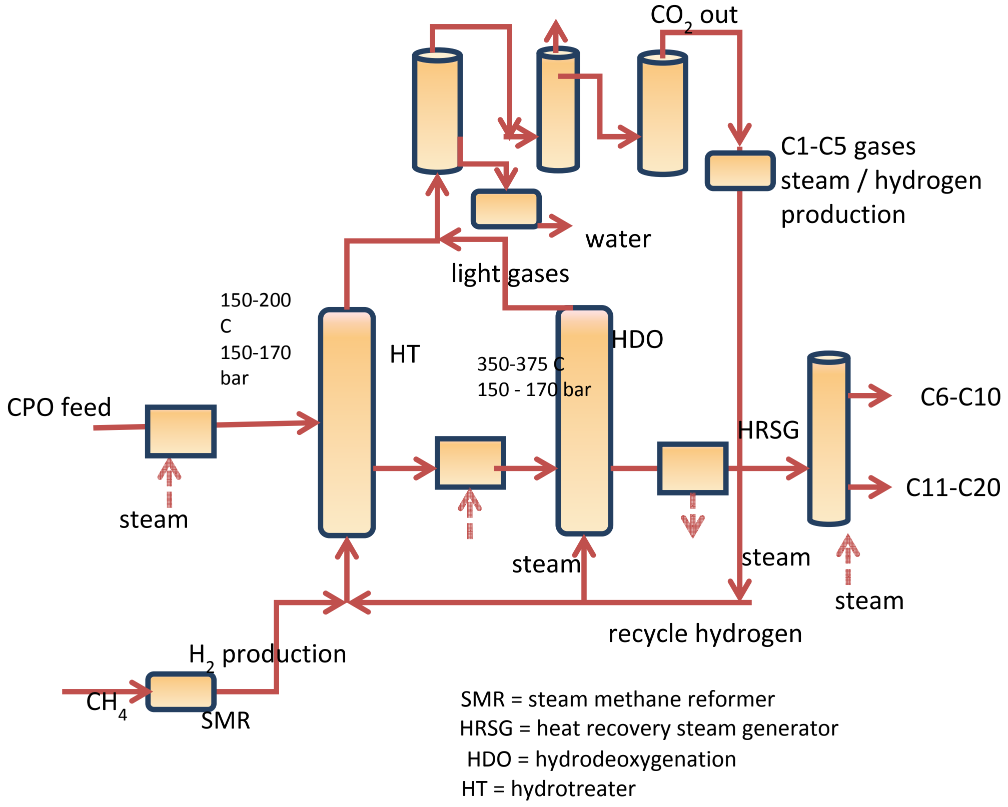
A two stage upgrading process concept of CP oils is proposed. In the 1st stage, the CP oil compounds are stabilized in order to prevent coking of the catalyst. The optimized reaction conditions have yet to be determined but have temperatures in the range of 150 - 250 C and hydrogen pressures in the range of 100 to 150 bar. The 2nd stage of the overall process concept is comprised of slowing raising the reactor temperatures to 350 - 375 C and this is where the hydrodeoxygenation (HDO) occurs. Depending on the catalyst and quality of the the CP oil feed, cracking reactions will also occur under these conditions.

Assuming that operating conditions can be found to stabilize the CP oil and that the conditions gradually increase in severity and coke formation is avoided, then the use of typical refinery catalysts such as NiMo or CoMo where the catalyst support has been modified to withstand the water partial pressures should be possible.

The conditions used in the hydrotreating of CP oils have been found to be significantly different than what is found in existing hydrotreating processes and separate units are used.

Subsequent to the hydrotreating of the CP oil, the off gases are separated and fed into the refinery gas treatment block, hydrogen is recovered and may be returned to the process; the water condensed and treated in waste water plant; CO2 released, light gases are recovered and fed into refinery network for steam/power production or SMR feed. Heat recovery is recovered in a HRSG to generate medium pressure steam.

Hydrogen is consumed in the upgrading at approximately 6-7 wt% of CP oil feed, which at a 73 wt% conversion is 9-10 wt% of hydrocarbon products.



7.4 MASS BALANCE

A preliminary mass balance from the experimental work carried out at Neste Oil is shown below.

	Calculated per 1 kg (dry) product	Calculated per 1 kg (dry feed) feed
	g	g
hydrogen	82	60
water	0	50
feed	1370	1000
Product oil	1000	730
Product gas	205	150
product water	178	130

The composition of the gas is roughly 93 wt% hydrocarbons with the remainder being carbon dioxide and carbon monoxide. This gas could be used for energy production or alternatively for hydrogen production as a feed in the SMR (steam methane reformer) thus reducing the carbon footprint of the product. Whether it is used for energy production or for hydrogen production it will replace an energy equivalent amount of natural gas. Roughly this is (0.15 x 45 MJ) / (0.73 x 43) = 0.22 MJ off gases /MJ product.

7.5 HYDROGEN CONSUMPTION

From the mass balance, we have 0.082 kg H2 consumed per kilogram product. This is (0.082 x 120) / (1 x 43) = 0.22 MJ H2 / MJ product. Hydrogen production efficiencies are on the order of 68-75% depending on the tupe of plant in question. Modern plants reach this higher efficiency level. This translates into 0.22 / 0.75 = 0.29 MJ methane require per MJ of produced product. This can be compared to the off gas heat content of 0.22 MJ / MJ of product.

7.6 GAS TREATMENT

Gases produced in the process are fed into the refinery gas treatment network where hydrogen is separated from the hydrocarbons and from the carbon dioxide This is normally performed by a combination of an amine wash and high pressure membranes.

Annex I

European Refineries and Hydrogen Production and Consumption

In 2012, there were 655 refineries worldwide, with a total capacity of around 4 400 million t/yr. The world's largest refining region is Asia (25 %), followed by North America and Europe (around 20 % each). ('Worldwide refineries -Capacities as of January 2012 Oil & Gas Journal/Dec. 5, 2011').

In Europe there is over production of certain petroleum products and although some European oil refineries have closed in the last 25 years there has been a progressive increase of crude oil processing capacity since the 1990s, mainly by ‘capacity creep’ (debottlenecking, improvements in equipment reliability and longer cycles between turnarounds) to cope with a 1 – 2 % increase in product demand per year in Europe.

Since 2005, there has been a stabilisation and even a slight decrease of the overall European demand. The crude oil capacity of the 106 plants operating in the EU-27 at the beginning of 2013 was approximately 1 billion tonnes per year. The average individual capacity of European sites was about 7.9 Mm3/yr, similar to the other parts of the world.

Hydrogen production has become a priority in current refinery operations due to the production of lower sulphur gasolin and diesel fuels together and the requirement of deeper hydrotreating of heavier and higher sulphur crudes. There is currently an increasing demand for hydrogen in European refining, due to an increased use of hydrocracking and hydrotreating. More hydrodesulphurisation is needed to achieve legislative requirements for lower sulphur content in fuels. There are no available statistics concerning the availability of excess hydrogen in oil refineries but based on the earlier analysis it can be concluded that there is no available reserve of hydrogen that may be used for catalytic pyrolysis oil feeds.

The main feedstock used in hydrogen production is methane with light refinery gas as a close second in some refineries. Olefins in he gas can cause problems by forming coke in the reformer and are converted to saturated compounds in the hydrogenator.

Current annual global hydrogen production is approximatley 50 million tonnes.

http://www.hydrogen.energy.gov/pdfs/hpep_report_2013.pdf

http://eippcb.jrc.ec.europa.eu/reference/BREF/FD_REF_July_2013online.pdf

Refineries with capacity > 50 k bbl 7 d; data taken from: 'Worldwide refineries - Capacities as of January 2012 Oil & Gas Journal/Dec. 5, 2011'   100 k bbl/d = 5 Mt/a

	k bbl/d
Austria	
Schwechat Refinery (OMV), 176,000 bbl/d (28,000 m3/d)	176
Azerbaijan	
Haydar Aliev Refinery (SOCAR), 160,000 bbl/d (25,000 m3/d)	160
Azerineftyag Refinery (SOCAR), 239,000 bbl/d (38,000 m3/d)	239
	399
Bosnia and Herzegovina	
Bosanski Brod Refinery Nestro, a subsidiary of JSC Zarubezhneft (Russia)	
Belarus	
Mozyr Refinery (Slavneft),[6] 95,000 bbl/d (15,100 m3/d)	95
Novopolotsk Refinery (Naftan), [7] 88,000 bbl/d (14,000 m3/d)	88
	183
Belgium	
Total Antwerp Refinery (Total), 360,000 bbl/d (57,000 m3/d)	360
ExxonMobil Antwerp Refinery (ExxonMobil), 333,000 bbl/d (52,900 m3/d)	333
Antwerp N.V. Refinery (Vitol), 35,000 bbl/d (5,600 m3/d)	35
Independent Belgian Refinery, Antwerp (Gunvor), 115,000 bbl/d (18,300 m3/d)	115
	843
Bulgaria	
LUKOIL Neftochim Burgas (LUKOIL), 208,000 bbl/d (33,100 m3/d)	208
Croatia	
Rijeka Refinery (INA), 90,000 bbl/d (14,000 m3/d)	90
Sisak Refinery (INA), 60,000 bbl/d (9,500 m3/d)	60
	150
Czech Republic	
Litvinov Refinery (Česká Rafinérská), 120,000 bbl/d (19,000 m3/d)	120
Kralupy Refinery (Česká Rafinérská), 80,000 bbl/d (13,000 m3/d)	80
	200
Denmark	
Kalundborg Refinery (Statoil), 110,000 bbl/d (17,000 m3/d)	110
Fredericia Refinery (Royal Dutch Shell), 68,000 bbl/d (10,800 m3/d)	68
	178
Finland	
Porvoo Refinery (Neste Oil Oyj), 206,000 bbl/d (32,800 m3/d)	206
Naantali Refinery (Neste Oil Oyj), 58,000 bbl/d (9,200 m3/d)	58
	264

France

Provence Refinery (Total), 155,000 bbl/d (24,600 m3/d)	155
Normandy Refinery (Total), 350,000 bbl/d (56,000 m3/d)	350
Flandres Refinery (Total), 160,000 bbl/d (25,000 m3/d) Closed	160
Donges Refinery (Total), 231,000 bbl/d (36,700 m3/d)	231
Feyzin Refinery (Total), 119,000 bbl/d (18,900 m3/d)	119
Grandpuits Refinery (Total), 99,000 bbl/d (15,700 m3/d)	99
Port Jérôme-Gravenchon Refinery (ExxonMobil), 270,000 bbl/d (43,000 m3/d)	270
Fos-sur-Mer Refinery (ExxonMobil), 140,000 bbl/d (22,000 m3/d)	140
Reichstett Refinery (Petroplus), 77,000 bbl/d (12,200 m3/d)	77
Berre L'Etang Refinery (LyondellBasell), 80,000 bbl/d (13,000 m3/d)	80
Fort de France Refinery (Total), 17,000 bbl/d (2,700 m3/d)	17
	1698

Germany

Schwedt Refinery (PCK Raffinerie(Shell/Rosneft/BP/AET), 210,000 bbl/d (33,000 m3/d)	210
Ingolstadt Refinery (Bayernoil(OMV/Agip/Rosneft/BP)), 262,000 bbl/d (41,700 m3/d)	262
Ingolstadt Refinery (Gunvor), 110,000 bbl/d (17,000 m3/d)	110
Ruhr Öl Refinery (Rosneft/BP), 266,000 bbl/d (42,300 m3/d)	266
Buna SOW Leuna Refinery (Total), 222,000 bbl/d (35,300 m3/d)	222
Wilhelmshaven Refinery (Hestya), idle 300,000 bbl/d (48,000 m3/d)	300
Rheinland Werk Godorf Cologne Refinery (Royal Dutch Shell), 190,000 bbl/d (30,000 m3/d)	190
Rheinland Werk Wesseling Cologne Refinery (Royal Dutch Shell), 160,000 bbl/d (25,000 m3/d)	160
Mineraloil Refinery Upper-Rhine (Karlsruhe) 285,000 bbl/d (45,300 m3/d)	285
Burghausen Refinery (OMV) 70,000 bbl/d (11,000 m3/d)	70
TOTAL Refinery Mitteldeutschland (Total) 227,000 bbl/d (36,100 m3/d)	227
Emsland Lingen Refinery (BP) 80,000 bbl/d (13,000 m3/d)	80
Holborn Europa Raffinerie GmbH Hamburg (Holborn) 100,000 bbl/d (16,000 m3/d)	100
Raffinerie Heide www.heiderefinery.com(Klesch) 90,000 bbl/d (14,000 m3/d)	90
	2572

Greece

Aspropyrgos Refinery (Hellenic Petroleum), 135,000 bbl/d (21,500 m3/d)	135
Elefsina Refinery (Hellenic Petroleum), 100,000 bbl/d (16,000 m3/d)	100
Thessaloniki Refinery (Hellenic Petroleum), 100,000 bbl/d (16,000 m3/d)	100
Korinth Refinery (Motor Oil Hellas), 100,000 bbl/d (16,000 m3/d)	100
	435

Hungary

Szazhalombatta Refinery (MOL), 161,000 bbl/d (25,600 m3/d)	161

Ireland

Whitegate Refinery (Phillips 66), 71,000 bbl/d (11,300 m3/d)	71

Italy	
Sarpom Trecate, Novara Refinery 200,000 bbl/d (32,000 m3/d)	200
Esso Augusta Refinery (ExxonMobil), 190,000 bbl/d (30,000 m3/d)	190
Rome Refinery (Total 77.5%/ERG 22.5%), 90,000 bbl/d (14,000 m3/d) Closed	90
Falconara Marittima Ancona Refinery (API), 85,000 bbl/d (13,500 m3/d)	85
Mantova Refinery (IESItaliana), 55,000 bbl/d (8,700 m3/d) Closed	55
Impianti Sud Refinery (ISAB ERG), 214,000 bbl/d (34,000 m3/d)	214
Impianti Nord Refinery (ISAB ERG), 160,000 bbl/d (25,000 m3/d)	160
Milazzo Refinery (Eni/KNPC) 80,000 bbl/d (13,000 m3/d)	80
Sannazzaro de' Burgondi Refinery (Eni) 160,000 bbl/d (25,000 m3/d)	160
Gela Refinery (Eni) 100,000 bbl/d (16,000 m3/d)	100
Taranto Refinery (Eni) 90,000 bbl/d (14,000 m3/d)	90
Livorno Refinery (Eni) 84,000 bbl/d (13,400 m3/d)	84
Porto Marghera Venice Refinery (Eni) 70,000 bbl/d (11,000 m3/d)	70
Cremona Refiney (Tamoil) 80,000 bbl/d (13,000 m3/d) Closed	80
Sarroch Refinery, Sardegna (Saras S.p.A.) 300,000 bbl/d (48,000 m3/d)	340
	1998
Kosovo	
Kulla Exim Refinery (Kulla Exim SH.P.K.)100,000 bbl/d (16,000 m3/d)	100
Lithuania	
Mazeikiu Refinery (Mazeikiu Nafta - PKN Orlen), 263,000 bbl/d (41,800 m3/d)	263
Macedonia	
OKTA Skopje Refinery (Hellenic Petroleum), 50,000 bbl/d (7,900 m3/d)	50
Netherlands	
Shell Pernis Refinery (Royal Dutch Shell), 416,000 bbl/d (66,100 m3/d)	416
Botlek (ExxonMobil) Rotterdam, 195,000 bbl/d (31,000 m3/d)	195
BP Rotterdam Refinery (BP), 400,000 bbl/d (64,000 m3/d)	400
Q8-KPE Refinery Europoort (Q8-Kuwait Petroleum Company), 80,000 bbl/d (13,000 m3/d)	80
Koch HC Partnership Refinery (Vopak Terminal Europoort BV) 80,000 bbl/d (13,000 m3/d)[14]	80
Vlissingen Refinery (Total/Lukoil) 149,000 bbl/d (23,700 m3/d)[15]	149
	1320
Norway	
Slagen Refinery (ExxonMobil), 110,000 bbl/d (17,000 m3/d)	110
Mongstad Refinery (Statoil), 200,000 bbl/d (32,000 m3/d)	200
	310
Poland	
Plock Refinery (PKN Orlen), 276,000 bbl/d (43,900 m3/d)	276
Gdansk Refinery (Grupa LOTOS), 210,000 bbl/d (33,000 m3/d)	210
	507,8

Portugal	
Porto Refinery (Galp Energia), 100,000 bbl/d (16,000 m3/d)	100
Sines Refinery (Galp Energia), 200,000 bbl/d (32,000 m3/d)	200
	300
Romania	
Arpechim Refinery Piteşti, (Petrom/OMV), 70,000 bbl/d (11,000 m3/d)	70
Astra Refinery (Interagro), 20,000 bbl/d (3,200 m3/d) Closed	20
Petrobrazi Refinery Ploieşti, (Petrom/OMV), 90,000 bbl/d (14,000 m3/d)	90
Petromidia Constanţa Refinery (Rompetrol), 100,000 bbl/d (16,000 m3/d)	100
Petrotel Lukoil Refinery Ploieşti, (LUKOIL), 68,000 bbl/d (10,800 m3/d)	68
Petrolsub Suplacu de Barcău Refinery (Petrom/OMV), 15,000 bbl/d (2,400 m3/d)	15
RAFO Oneşti (Calder A), 70,000 bbl/d (11,000 m3/d)	70
Steaua Romană Câmpina Refinery (Omnimpex Chemicals), 15,000 bbl/d (2,400 m3/d)	15
Vega Ploieşti Refinery (Rompetrol), 20,000 bbl/d (3,200 m3/d)	20
	468
Russian Refineries Europe	
Syzran Refinery (Rosneft), 213,400 bbl/d (33,930 m3/d)	213
Novokuibyshevsk Refinery (Rosneft), 191,500 bbl/d (30,450 m3/d)	192
Kuibyshev Oil Refinery (Rosneft), 139,800 bbl/d (22,230 m3/d)	140
Salavatnefteorgsintez Refinery (Gazprom, Salavat), 250,000 bbl/d (40,000 m3/d)	250
Volgograd Refinery (LUKOIL), 193,000 bbl/d (30,700 m3/d)	193
Ukhta Refinery (LUKOIL), 72,000 bbl/d (11,400 m3/d)	72
Perm Refinery (LUKOIL), 235,000 bbl/d (37,400 m3/d)	235
NORSI-oil (LUKOIL, Kstovo), 292,000 bbl/d (46,400 m3/d)	292
Ryazan Refinery (Rosneft), 253,000 bbl/d (40,200 m3/d)	253
Orsk Refinery (Russneft), 159,000 bbl/d (25,300 m3/d)	159
Chernigov Refinery (ZAO "Chernigovskiy Npz"), 159,000 bbl/d (25,300 m3/d)	159
Saratov Refinery (Rosneft), 108,000 bbl/d (17,200 m3/d)	108
Moscow Refinery 213,000 bbl/d (33,900 m3/d)	213
Kirishi Refinery (Surgutneftegas), 337,000 bbl/d (53,600 m3/d)	337
YaNOS Yaroslavl Refinery (Slavneft), 132,000 bbl/d (21,000 m3/d)	132
Krasnodar Refinery (Russneft), 58,000 bbl/d (9,200 m3/d)	58
Tuapse Refinery (Rosneft), 85,000 bbl/d (13,500 m3/d)	85
Nizhnekamsk Refinery (TAIF), 14,000 bbl/d (2,200 m3/d)	14
Ufa Refinery (Bashneft), 190,000 bbl/d (30,000 m3/d)	190
Novo-Ufa Refinery (Bashneft), 380,000 bbl/d (60,000 m3/d)	380
Ufaneftekhim Refinery (Bashneft), 250,000 bbl/d (40,000 m3/d)	250
	3925
Asia	
Achinsk Refinery (Rosneft), 131,000 bbl/d (20,800 m3/d)	131
Angarsk Petrochemical Refinery (Rosneft), 384,000 bbl/d (61,100 m3/d)	384
Khabarovsk Refinery (Alliance), 85,000 bbl/d (13,500 m3/d)	85
Komsomolsk Refinery (Rosneft), 120,000 bbl/d (19,000 m3/d)	120
Nizhnevartovsk Refinery (Rosneft), 25,100 bbl/d (3,990 m3/d)	25
Omsk Refinery (Gazprom Neft), 380,000 bbl/d (60,000 m3/d)	380
	1125

Slovakia	
Slovnaft Bratislava Refinery (MOL), 110,000 bbl/d (17,000 m3/d)	110
Petrochema Dubová Refinery (russian investors), Petrochema	
Spain	
Bilbao Refinery (Repsol YPF), 220,000 bbl/d (35,000 m3/d)	220
Puertollano Refinery (Repsol YPF), 140,000 bbl/d (22,000 m3/d)	140
Tarragona Refinery (Repsol YPF), 160,000 bbl/d (25,000 m3/d)	160
A Coruña Refinery (Repsol YPF), 120,000 bbl/d (19,000 m3/d)	120
Cartagena Refinery, (Repsol YPF), 220,000 bbl/d (35,000 m3/d)	220
Tenerife Refinery (CEPSA), 90,000 bbl/d (14,000 m3/d)	90
Palos de la Frontera Refinery (CEPSA), 100,000 bbl/d (16,000 m3/d)	100
Gibraltar-San Roque Refinery (CEPSA), 240,000 bbl/d (38,000 m3/d)	240
Castellon Refinery (BP), 100,000 bbl/d (16,000 m3/d)	100
	1390
Sweden	
Gothenburg Refinery (78,000 bpd refining capacity) (st1)	78
Nynäshamn Refinery (90,000 bpd refining capacity) (Nynas)	90
Gothenburg Refinery (125,000 bpd refining capacity) (Preem)	125
Lysekil Refinery (220,000 bpd refining capacity) (Preem)	220
	513
Switzerland	
Cressier Refinery (Vitol), 68,000 bbl/d (10,800 m3/d)	68
Collombey-Muraz Refinery (Tamoil), 45,000 bbl/d (7,200 m3/d)	45
	113
Turkey	
Central Anatolian Refinery (Tüpraş), 100,000 bbl/d (16,000 m3/d)	100
Izmit Refinery (Tüpraş), 226,000 bbl/d (35,900 m3/d)	226
Aliaga Refinery (Tüpraş), 200,000 bbl/d (32,000 m3/d)	200
Batman Refinery (Tüpraş) 22,000 bbl/d (3,500 m3/d)	22
	548
Ukraine	
Odessa Refinery (LUKOIL), 70,000 bbl/d (11,000 m3/d)	70
LINOS Refinery (TNK-BP), 320,000 bbl/d (51,000 m3/d)	320
Kherson Refinery (Alliance), 36,000 bbl/d (5,700 m3/d)	36
Kremenchug Refinery (Ukrtatnafta) 368,500 bbl/d (58,590 m3/d)	369
Drogobych Refinery (Pryvat) 40,000 bbl/d (6,400 m3/d)	40
Neftekhimik Prikarpatya Nadvirna Refinery (Pryvat) 39,000 bbl/d (6,200 m3/d)	39
	874
United Kingdom	
England Fawley Refinery (ExxonMobil), 330,000 bbl/d (52,000 m3/d)	330
Humber Refinery (Phillips 66), 221,000 bbl/d (35,100 m3/d)	221
Lindsey Oil Refinery (Total), 223,000 bbl/d (35,500 m3/d)	223
Stanlow Refinery (Essar Oil), 272,000 bbl/d (43,200 m3/d)	272
Scotland Grangemouth Refinery (Ineos and PetroChina), 205,000 bbl/d (32,600 m3/d)	205

Wales Milford Haven Refinery (Murco),135,000 bbl/d (21,500 m3/d)	135
Pembroke Refinery (Valero), 215,000 bbl/d (34,200 m3/d)	215
	1601