Fuels from Waste and Hydrogen – The HAW Hamburg Approach

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Abstract:

The HAW Hamburg has developed an innovative reactive distillation technique, called READiTM process, in cooperation with the partner company Nexxoil. This process, a combination of non-catalytic thermal cracking and deoxygenation, offers the chance to convert a wide range of waste based raw materials into bio-oils. Characteristics of these bio-oils are low viscosity and low oxygen content. Due to that, they can be processed into liquid hydrocarbons as a basis for drop-in fuel production with comparatively little effort by hydrotreating. In the current READ-iTM-PtL project such a two-step approach of READiTM process (1st step) and hydrotreating (2nd step) is applied to use cooking oil (UCO). In this case, the inter-mediate bio-oil is called CVO (Cracked Vegetable Oil); the final hydrotreated product is called HCVO (Hydrotreated Cracked Vegetable Oil). Within this project a technical prototype plant with a capacity of 2 tons per week is to be built and operated.

JEL Classification: Q01, Q16, Q56

Keywords: Advanced alternative fuels, renewable fuels, biofuels, waste-based fuels, solvolytic reactive distillation.
1 Introduction

Approximately 95% of the global transport sector is still based on liquid fuels (IEA, 2017). These liquid fuels, such as diesel fuel, gasoline or jet fuel, are mainly pure hydrocarbons. Main reasons for this are very high energy density (see Fig. 1) as well as easy handling, transportation and storage at ambient temperature and pressure conditions. An ideal scenario would be the replacement of fossil hydro-carbon fuels by renewable alternative hydrocarbon fuels in so-called drop-in qual-ity. In this case, the alternative fuels would be totally miscible with conventional fuels without any blend-walls, so that the existing infrastructure and engines could be used without any changes. Thus, advanced alternative liquid fuels in drop-in quality will gain impor-tance for rapid reduction of green-house gas (GHG) emis-sions in future mobility. These alternative fuels should not compete with food, but be based on waste and re-newable energy sources.

![Figure 1: Energy density of different energy carriers in the transport sector (Aatola et al., 2008; Willner, 2011; Fritsche et al., 2012; DEHEMA, 2018; Fraunhofer, 2017)](image)

HVO = Hydrotreated Vegetable Oil, LNG = Liquified Natural Gas,
CNG = Compressed Natural Gas

One approach to a solution is the conversion of waste-based resources into liquid hydrocarbons. There are already well-known concepts for this. One is the direct one-step catalytic hydrotreating of oils and fats producing so-called HVO (Hy-drotreated Vegetable Oil). HVO products are already in the market (Aatola et al., 2008; DBFZ, 2017; Honkanen, 2019). Another established concept is the conver-sion of various feedstocks into liquid hydrocarbons via synthesis gas and Fischer-Tropsch (FT) syn-thesis. This concept is referred to as XtL (Resource X to Liquid) such as GtL (Gas to Liquid), BtL (Biomass to Liquid), WtL (Waste to Liquid) and PtL (Power to Liquid).
A review on advanced alternative drop-in fuel approaches including HVO, XtL and others is given by a DECHEMA position paper (DECHE-MA, 2018).

The quality of the hydrocarbon products of these concepts are very good. But there are still some challenges to be tackled, for example relatively high production costs (Kasten and Timpe, 2019; Ziem-Milojevic, 2019; Howes, 2020). In this respect HVO has advantages over XtL, but is still significantly more expensive than conventional fuels (Howes, 2020). Moreover, a specific problem of HVO is the lack of flexibility with regard to usable raw materials, as it is restricted to oils and fats or fatty acids. In addition, the raw materials for HVO production must be refined and cleaned so that the catalysts used are not deactivated by impurities (DBFZ, 2015).

Thus, there is potential for further improvement. In order to produce renewable hydrocarbons in sufficient quantities worldwide, more cost-effective processes with the widest possible range of applications are sought both on the raw material side and on the product side.

For about ten years, such a process, which offers this potential of flexibility with comparatively low process costs, has been researched and developed at the HAW Hamburg (Hamburg University of Applied Sciences) in cooperation with Nexxoil (Nexxoil GmbH, www.nexxoil.com). Nexxoil is a spin-off technology company of the HAW Hamburg. This is the so-called READiT process, which can be used to produce high-quality bio-oils as a renewable petroleum substitute on the basis of residual and waste materials. Various input materials such as used cooking oil (UCO), used ship oils or plastic waste have already been successfully tested in lab scale.

A two-step process set-up, consisting of the READiT process as a first step and a subsequent hydrotreating step, can produce drop-in fuel products. This article presents results of investigations on this concept, using the example of the conversion of UCO into such fuels.

2 X-Energy READiT-PtL project of the HAW Hamburg

The READiT-PtL project is a subproject of the joint X-Energy project of the HAW Hamburg (HAW, 2019). Project partner is Nexxoil. The current first phase of the project (2018 to 2021) includes lab scale investigations on a two-step conversion of UCO into renewable fuels and the construction of a READiT process prototype plant with a capacity of 2 tons per week. In the planned second project phase (2021 to 2024) the process concept is to be transferred to another source of raw material such as plastic waste.

Fig. 2 shows the two-step concept of the conversion of UCO into drop-in fuels, which is to be investigated and realized within the READiT-PtL project of the HAW Hamburg. The target fuel will initially be a renewable drop-in diesel fuel product.
But the liquid hydrocarbon mixture produced can in principle also be processed into renewable drop-in products for all other known types of fuel, such as gasoline and jet fuel, as well as renewable hydrocarbons for the petrochemical industry, such as naphtha.

In the first step, the READiTM process, the raw material is upgraded to a high-quality bio-oil with reduced viscosity and oxygen content, mainly by cracking and deoxygenation. In the second step the intermediate bio-oil is upgraded by treating with pressurized hydrogen to a pure almost oxygen-free liquid hydrocarbon product. The hydrogen should be produced by renewable power via electrolysis of water. In that sense the two-step approach is a PtL (Power to Liquid) concept, indicated by the project acronym READiTm-PtL.

The first step, the READiTm process, as illustrated in Fig. 3, works according to the innovative principle of reactive distillation, which is reflected in the process designation READiTm (Augustin 2016, Augustin et al. 2016). In this process, a highermolecular organic starting material is thermally stressed and cracked in the absence of oxygen in a low-volatile liquid solvent as reaction medium, the so-called sump phase. The solvent is also involved in cracking and radical stabilization reactions. Thus, it is solvolytically acting with the basic idea of suppressing coking reactions. Due to the use of a solvolytic reaction medium similar to corresponding approaches in the context of direct liquefaction of lignocellulosic biomass, the process is also referred to as solvolysis (Isa et al., 2018; Lange, 2018; Ghosh and Haverly, 2019) or solvo-thermal processing (IEA, 2016). Accordingly, the principle of the READiTm process is also called “Solvolytic Reactive Distillation” (SRD).
In the reactor of the READiT process, thermal cracking reactions convert the large molecules of the raw material into medium to short-chain molecules as a product. Due to their increased vapor pressure, the cracking products can evaporate from the sump phase and thus leave the reactor by distillation via the gas-vapor phase. After subsequent cooling and partial condensation of the gas-vapor phase outside the reactor, a condensate and a remaining gas phase are obtained. The gas phase is removed and could later be used as an energy source to heat the reactor. The condensate is mainly an organic product phase, the so-called bio-oil as a petroleum substitute target product of the first step, and usually also a small amount of water phase, that is immiscible with the bio-oil.

Due to the innovative combination of reaction and distillation the bio-oil is free of undesired long-chain heavy-oil molecules. The reason for this is that large molecules stay in the reactor until they are cracked down into the target chain-length corridor. As soon as the molecules have reached the desired chain-length they are removed from the reactor by distillation. This prevents them from undesired further cracking which would result in higher amounts of too small molecules in particular in the gas-product range. In that sense the reactive distillation approach is a self-controlling residence time optimization concept.
These effects of reactive distillation are advantageous for cost reduction by maximizing the yield of the liquid product in the desired chain-length range and by minimizing the effort for further upgrading of the liquid product by refining.

The READiTM process is a fully continuous approach. A particular challenge is the stabilization of the sump phase in continuous long-term operation. In order to minimize process costs, no externally provided solvents should be used, which would be consumed in the process and would have to be purchased again and again. The central idea of the process is that the sump phase is continuously regenerated by continuously reproducing it from oligomeric intermediate products of the cracking process. In this way the sump phase should be self-regenerating. Preliminary tests on refined rape-seed oil as a model substance for triacylglycerol mixtures have shown that the sump phase develops as intended towards a stable state over time (Augustin, 2016), with the exception of the formation of small proportions of solid residues (char). These solids must be separated continuously to prevent them from accumulating in the reactor.

Figure 4: Simplified reaction scheme of the 1st step, the READiTM process (Sievers, 2013)

UCO = Used Cooking Oil, CVO = Cracked Vegetable Oil

Fig. 4 illustrates the reaction scheme of the first step, the READiTM process, addressing cracking and deoxygenation. Deoxygenation reactions, mainly decarbonylation and decarboxylation supplemented by some water formation, reduce the oxygen content significantly. In case of UCO as feedstock, the oxygen content is reduced from 11 wt.% (weight percent) in the UCO to a low level of 3 to 5 wt.% in the intermediate bio-oil product, here called CVO (Cracked Vegetable Oil). The residual oxygen content is mainly bound in organic acid groups (Sievers, 2013).
The significant oxygen reduction in the first step without using catalysts or hydrogen is advantageous in terms of cost reduction, because beforehand oxygen reduction means lowering the hydrogen demand for the subsequent hydrotreating in the second step aiming at pure hydrocarbon products. A specific economic advantage of not using catalysts in the first step is that the process is very resistant to impurities and therefore cheap low-quality raw materials can be processed.

A flow sheet of the second step, the catalytic hydrotreating of the bio-oil, is shown in Fig. 5 according to an experimental set-up of the Freiburg University of Technology (Endisch et al., 2013). There, typically 60 bar hydrogen pressure is applied in a temperature range between 230 and 360 °C for reducing the oxygen content to below 1 wt.%. The reactions are supported by catalysts in a trickle-bed continuous flow reactor. In case of using CVO as bio-oil, the resulting hydrotreated product is called HCVO (Hydrotreated Cracked Vegetable Oil).

Unpublished tests on the continuous bench-scale hydrotreating of CVO at 60 bar and 320 °C at the Institute for Energy Process Engineering and Chemical Engineering (IEC) of the Freiburg University of Technology came to the result, that the hydrogen demand of CVO hydrotreating is 1.3%, based on the initial feedstock UCO, instead of about 3% in case of direct one-step hydrotreating of oils and fats. Literature is giving similar results for the hydrogen demand of direct hydrotreating of triacylglycerol oils, such as 2.7% for rapeseed oil or 2.5% for jatropha oil under ideal laboratory conditions (Endisch et al., 2013) or 3.5% for jatropha oil as an assumption for real industrial process conditions (DBFZ, 2017).
The verification of the reduced hydrogen demand confirms the expected cost-reducing benefit of the two-step approach of this project. Further intensive re-search on CVO hydrotreating has been done at HAW Hamburg, applying the inno-vative reaction concept of reactive stripping, showing that standard hydrotreating catalysts are suitable (Sievers, 2013; Sievers et al., 2014; Baldauf et al., 2014; Bal-dauf et al., 2016; Baldauf, 2016; Baldauf et al., 2017). In these investigations, the mode of hydrotreating processing was gradually transferred from batch operation via semi-continuous operation to fully continuous operation (Baldauf, 2016).

A reaction scheme of the hydrotreating step is illustrated in Fig. 6 (Sievers, 2013; Baldauf, 2016). The pressurized hydrogen supported by catalysts saturates the double bonds, so-called hydrogenation, and removes residual oxygen by water formation, so-called hydrodeoxygenation, accompanied by some further decar-bonylation and decarboxylation (Baldauf et al., 2016). Cracking losses during the hydrotreating can be minimized. Accordingly, yields of up to 95% of HCVO can be achieved, based on incoming CVO (Baldauf, 2016).

Figure 6: Simplified reaction scheme of the 2nd step, the hydrotreating (Sievers, 2013; Bal-dauf, 2016)

H2 = Hydrogen, CVO = Cracked Vegetable Oil, HCVO = Hydrotreated Cracked Vegetable Oil

The general target of hydrotreating bio-oils is producing renewable hydrocarbon products, which are chemically and physically equivalent to fossil fuels or petro-chemicals. Basically, the hydrotreating of oils is an established and mature refinery process. But in case of processing bio-oils, there is some adjustment of the standard refinery hydrotreating procedure necessary due to the residual oxygen content in the bio-oil. This shall be subject of investigation in further projects.
Fig. 7 shows pictures and some data of the feedstock (UCO), the intermediate product (CVO) and the hydrocarbon product (HCVO) for comparison. Obviously, the CVO is a clean transparent distillate product from the dirty feedstock UCO. While the CVO has still some reddish color, the HCVO is colorless clear. According to the decreasing oxygen content, the calorific value is increasing from UCO (37 MJ/kg) via CVO (42 MJ/kg) to HCVO (44 MJ/kg). While the viscosity of UCO is too high for standard fuels, the viscosity of both CVO and HCVO is well within the target corridor.

<table>
<thead>
<tr>
<th></th>
<th>UCO</th>
<th>CVO</th>
<th>HCVO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>37 MJ/kg</td>
<td>42 MJ/kg</td>
<td>44 MJ/kg</td>
</tr>
<tr>
<td>Oxygen</td>
<td>11 wt.%</td>
<td>3-5 wt.%</td>
<td>0 wt.%</td>
</tr>
<tr>
<td>Viscosity (40 °C)</td>
<td>44 mm²/s</td>
<td>3.8 mm²/s</td>
<td>2.3 mm²/s</td>
</tr>
</tbody>
</table>

Figure 7: Feedstock (UCO), intermediate product (CVO) and hydrocarbon product (HCVO)

UCO = Used Cooking Oil, CVO = Cracked Vegetable Oil, HCVO = Hydrotreated Cracked Vegetable Oil

The HCVO product can serve as a basis for the production of standard-compliant drop-in fuels. It can be separated into a naphtha fraction and a diesel fraction by rectification (multistage distillation), a standard procedure in petroleum refining. The naphtha fraction in the boiling range from 80 °C to 180 °C can be both a basic material for the chemical industry and a basis for gasoline fuel production via further upgrading steps such as isomerization for improving the octane number. The diesel fraction in the boiling range from 180 °C to 360 °C is the main part of the HCVO with a share of about 80 to 90%. It can be used as a blending component for diesel fuel without any further modification. Its cetane number is expected to be high, indicated by an analyzed high cetane index of 70.7. Such a high cetane value suggests that the combustion of HCVO diesel fraction will be significantly cleaner than that of conventional diesel fuel. The viscosity of the diesel fraction measured at 40 °C is 2.9 mm²/s, being well within the EN 590 standard diesel fuel range from 2.0 to 4.5 mm²/s. Its density measured at 15 °C is 804 kg/m³, being closer to the EN 590 standard range from 820 to 845 kg/m³ than the density of diesel products from both direct one-step
catalytic hydrotreated oils or fats and synthetic fuels via synthesis gas with Fischer-Tropsch (FT) synthesis such as GtL (Gas to Liquid), BtL (Biomass to Liquid) or PtL (Power to Liquid) approaches, which is reported to be 775 to 785 kg/m³ and 770 to 785 kg/m³ respectively (Aatola et al., 2008).

It can therefore be expected that the diesel fuel blending percentage of the HCVO product can be higher than that of both one-step hydrotreating products and products from XtL (GtL, BtL or PtL), if one is to remain within the EN 590 standard.

Fig. 8 gives the overall mass balance and the energy shares of educts and products of the HCVO production process line. The hydrogen demand is low with the already mentioned 1.3%. The yield of the target product HCVO is about 75%. There is some char produced in the order of 4%, which can be upgraded and used as a soil conditioner giving the very promising chance of even negative CO2 emissions. The exhaust gas, with a share of appr. 13%, contains energy which can be used to heat the process, in particular the reactor of the first process step. The water phase as the rest, still containing some 20 to 25% water-soluble organic matter, could later be used as a raw material for biogas production.

<table>
<thead>
<tr>
<th>UCO</th>
<th>H₂</th>
<th>→</th>
<th>HCVO</th>
<th>+</th>
<th>Char</th>
<th>+</th>
<th>Ex.gas</th>
<th>+</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>100</td>
<td>1,3</td>
<td>75</td>
<td>4</td>
<td>13</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy%</td>
<td>100</td>
<td>4</td>
<td>88</td>
<td>3</td>
<td>6</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 8: Overall mass balance and energy shares of educts and products

UCO = Used Cooking Oil, H₂ = Hydrogen, HCVO = Hydrotreated Cracked Vegetable Oil, Ex.gas = Exhaust gas

The energy% values in Fig. 8 show the energy shares of educts and products in terms of calorific values, based on the feedstock energy. The missing values for an energy balance are the energy demand for the process in the order of 5% on the left side and the energy losses in the order of 12% on the right side, again both based on the feedstock energy. The energy demand is mainly needed to heat the reactor of the first step of the process, the CVO bio-oil production step. As the exhaust gas contains some 6% of energy, this is enough to cover the process energy demand of about 5%, coming close to energy self-sufficient operation.

Fig. 9 illustrates the planned test plant in technical scale with a capacity of 2 tons per week. Construction and commissioning of this plant at the HAW Hamburg is part of the ongoing X-Energy READiTM-PtL project (HAW, 2019). The technology readiness level (TRL) of this plant will be TRL 6 according to the definition of EU Horizon 2020. The volume of the reactor for CVO production in this test plant will be around 200 liters. The space required corresponds to about two containers.
The objectives of the READiTM-PtL project are
- to verify both process steps of the two-step technology, the READiTM process step and the hydrotreating step,
- to evaluate the suitability of these process steps for integration into real renewable energy systems with fluctuating power supply and
- to estimate the economic efficiency.

The concrete main objective is the further development of the READiTM process for the first part of the two-step concept as a key technology for the economic efficiency of the overall concept. The READiTM process is to be scaled up from TRL 5 to TRL 6, resulting in a functional 2 tons per week prototype plant. Finally, the scaling to TRL 7 is to be prepared.

3 Conclusion and acknowledgement

First results of the ongoing READiTM-PtL project of the HAW Hamburg in cooperation with the partner company Nexxoil confirm some cost-reducing effects of the two-step approach for the conversion of waste fats and oils into pure liquid hydrocarbon products under investigation, if compared with the direct one-step catalytic hydrotreating. Some of these advantages could be:

- As the first step, the READiTM process does not use any catalysts, the process is robust against contaminants. Thus, cheap unpurified low-quality raw materials can be processed.
- The hydrogen demand can be reduced to less than half, or more than twice as much fuel can be produced with a certain amount of available hydrogen.
- The density of the diesel fraction of the hydrocarbon product HCVO is higher and thus closer to the EN 590 standard range than that of both direct one-step
hydrotreating products and XtL products via synthesis gas with FT synthesis. It is therefore to be expected that it will be possible to produce blends with higher HCVO contents that remain within the limits of EN 590.

Preliminary tests in lab scale have shown, that the READiTM process can be applied to the conversion of other raw material such as plastic waste. In a follow-up project this is to be verified in a modified 2 tons per week prototype test plant.

The authors thank the German Federal Ministry of Education and Research for funding the project. Furthermore, they thank Thomas Kuchling and Andrej Awgustow from the Institute for Energy Process Engineering and Chemical Engineering (IEC) of the Freiberg University of Technology (TU Bergakademie Freiberg) for investigating the hydrotreating for the conversion of CVO from the READiTM process step into a HCVO product.

4 References


