Hydroprocessing of **renewable feedstocks** - challenges and solutions

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Driven by recent changes to legislation, particularly in the EU and USA, hydroprocessing renewable feedstocks is becoming more commonplace. Other countries are also looking at legislation to reduce CO_2 emissions and the reliance of refineries on fossil fuels.

Refineries have been processing fossil fuels for more than a century. In comparison, converting renewables into transport fuels is relatively recent and comes with a new set of technical challenges, including:

- A large number of exothermic reactions along with a high consumption of hydrogen
- The risk of corrosion due to a high acid number, a high chlorine content and the presence of oxygenated compounds
- Pressure drop issues and eventual catalyst deactivation due to the presence of contaminants such as silicon and phosphorus
- The impact on the density and cold flow properties of the end product, which might then require additional processing
- The ability to secure a reliable supply of renewable feedstocks of sufficient quality

Challenges such as these require customized solutions which take into account the:

- Specific needs of each refinery
- Quality of the end product
- Nature of available feedstocks
- Availability of hydrogen
- Ease of integration with existing refinery units

For processing renewable feedstocks, Topsoe's solutions provide full feedstock flexibility, enabling refineries to produce clean fuels from a wide range of feeds, including vegetable oil, animal fat, used cooking oil, pyrolysis oil, and crude tall oil.

Topsoe has developed guard catalysts to handle contaminants and ensure full cycle length. Since the cloud point of renewable fuels is higher than fossil fuels, dewaxing becomes extremely important. We have responded by developing a new generation of dewaxing catalysts that improve the cold flow properties of renewable fuels by selective isomerization while minimizing loss of yield.

Our constant research and development has pushed the limites of catalyst technology while optimizing process design. As a result, we have become the market leaders in hydroprocessing renewable feedstocks for the production of almost any type of fuel.

Introduction

The transport sector is expected to experience significant growth in the coming years. Because of this, many countries have set ambitious targets to increase their use of renewable energy in an effort to curb rises in CO_2 emissions[1]. One of the measures they can take to help meet these targets is to legislate for the use of renewable feedstocks in the production of transport fuels. There is a variety of types of renewable feedstocks, including[2]:

- Oilseed crops
- Grains and sugar crops
- Biomass from waste, used cooking oils, animal fats, tires, etc.
- Ligno-cellulosic biomass from agricultural residues, algae, trees, and grasses

Table 1 below shows the three classes of conversion process capable of upgrading biomass to transport fuels.

The process for hydrotreating fatty acid-based feedstocks, such as vegetable oils and animals fats, is already well understood[3]. In fact, refineries all over the world are already hydrotreating these feedstocks, which accounted for 4% of the global production of renewable transport fuel in 2016[4].

However, objections to allocating farmland to produce “food as fuel” are likely to result in regulations limiting the use of fatty acid-based feedstocks. In the EU, for example, the so-called RED II legislation (Renewable Energy Directive for 2021-2030) aims to phase out high-ILUC (Indirect Land Use Change) crop-based biomass such as palm by 2030. It also limits the processing of used cooking oils and animal fats to 1.7% of total transport fuel production[5].

Fortunately, there are alternatives. Pyrolysis produces biocrudes that can be further hydrotreated using catalytic fast pyrolysis[6] and catalytic fast hydropyrolysis[7]. And a lot of work has been done on testing hydrothermal liquefaction to produce biocrudes – and demonstration units are currently under construction[8].

TABLE 1
Possible steps to convert biomass into transport fuels[1,2].

Chemical	Biological	Thermochemical
Transesterification	Conventional alcohol fermentation	Pyrolysis
Hydrotreating	Enzymatic hydrolysis and fermentation	Gasification
Hydrotreating	Anaerobic digestion	Hydrothermal liquefaction

The challenges of hydrotreating renewable feedstocks

Compared to fossil-based feedstocks, processing renewable feedstocks present some new challenges. This section unwraps the most important of these.

Corrosion

Vegetable or tall oils may contain high amounts of free fatty acids which can cause severe corrosion in pipes, heat exchangers, reactors, and other equipment. Chlorine present in the feedstock will be converted into hydrogen chloride in the hydrotreating reactor, which can cause corrosion in both the reactor effluent stream and the sour water unit. Carbonic acid is formed in the reactor effluent due to the presence of water and carbon dioxide. All of these factors have a profound effect on the design and the materials used in the construction of reactors for processing renewable feedstocks.

High hydrogen consumption

Large amounts of hydrogen are required to upgrade renewable feedstocks (300-400 Nm^3/m^3 of hydrogen is typically required to achieve a 100% renewable feed). This means you need a higher volume of make-up hydrogen and quench gas flow, even for co-processing relatively small amounts of renewable feedstock.

Because of this, it is crucial to check the refinery's hydrogen balance in order to avoid lowering unit capacity.

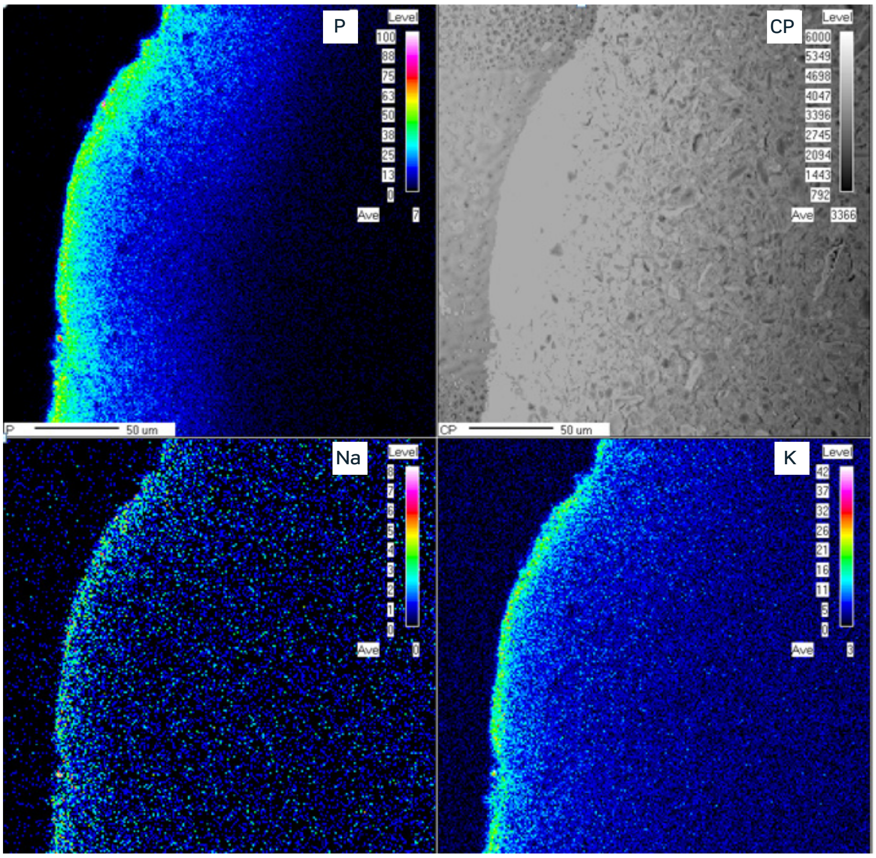

Figure 1. SEM picture of a high phosphorus-containing crust around a guard catalyst from a commercial unit processing 50% renewable feedstock.

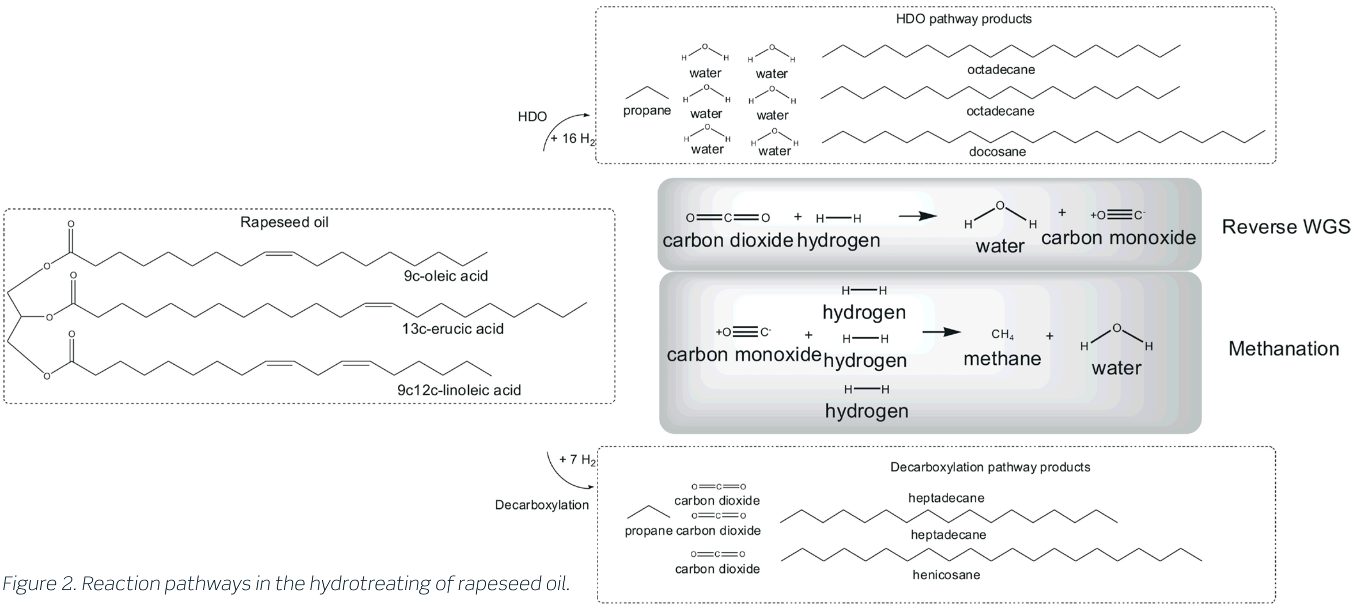

Figure 2. Reaction pathways in the hydrotreating of rapeseed oil.

Deactivation
Contaminants in renewable feedstocks, such as phosphorus, alkali metals, and alkaline earth metals, are known to cause operating problems[9]. For example, it has been reported that a build up of phosphate glass can cause pressure drops and accelerate catalyst deactivation. And phosphorus will almost certainly coat the external surface of catalysts and block the pores, as shown in Figure 1 on page 3. Once phosphate glass is formed, catalyst particles begin to adhere to each other. As the void slowly fills up, the likelihood of a pressure drop build-up rises.

This is why it is so important to specify a precise ceiling for the concentrations of each contaminant allowed for each feedstock.

Analyses of contaminants
Topsoe coordinated a qualitative round-robin study in 2018 involving 12 laboratories[10]. Each laboratory received three samples of renewable feedstocks – vegetable oil, animal fat, and pyrolysis oil. Adhering closely to international standards, they carried out a large number of analyses, including:

- Elemental analysis (C, H, N, S, O)
- Physico-chemical properties (SG, cloud point, pour point, TAN, water content)
- Contaminants (Al, Ca, Fe, K, Na, Mg, P, Si, Zn)

As you can see in Table 2, the laboratories observed large deviations in their results, especially for animal fat and pyrolysis oil. This suggests that significant work needs to be done on improving the reproducibility of the tests. And it reminds us that the processing of renewable feedstocks is still a relatively new field.

Feed supply
For many refineries interested in processing renewable feedstocks, feed supply is key. They are rightly concerned about questions such as:

- Does the potential supplier understand the market in sufficient depth, especially in terms of pricing, availability, and diversity?
- How stable is the quality of the feedstock?
- Is a regular, reliable supply available at all times?
- Will the feedstock be pretreated before delivery, or does it need to be pretreated on site?
- Can the supplier meet the company's criteria for sustainability?

Product properties
As you can see in Figure 2 on page 3, when triglycerides are hydrotreated, the resulting products are mostly n-paraffins. These exhibit poor cold flow properties, which is particularly critical if the target fuel is Arctic diesel. Because of this, dewaxing becomes necessary when co-processing exceeds 5-10%, depending on the properties of the fossil-based feedstock and the nature of the renewable feedstock.

TABLE 2
Evaluation of the results of the round-robin study[a].

	Vegetable oil	Animal fat	Pyrolysis oil
N	1 outside repro.	0 outside repro.	outside repro.
S	1	2	4
H	1	3	2
O	Not enough measurements to conclude		
C	1	0	4
SG	1	1	1
Cloud point	0	1	N.A.
Pour point	0	0	1
Water	3	1	6
TAN	1	0	3
Al	+	+	-
Ca	+	-	-
Fe	+	-	-
K	+	-	+
Na	+	-	-
Mg	+	+	-
P	+	-	-
Si	+	+	-
Zn	+	+	-

[a]For elemental analysis and physico-chemical properties, the number of data points outside the reproducibility limits is written down. For contaminants, the evaluation is more qualitative. The sign "+" was given when the data were in good agreement (no deviations) or with few outliers. The sign "-" was given when significant deviation was visible.

HydroFlex™ Flexible technologies for upgrading any feedstock

Hydroprocessing renewable feedstocks is complex. From process design to choosing the optimal catalyst technology, there are many factors to consider.

The first critical step is to decide exactly which product you want to end up with. Diesel or jet fuel? If you are considering diesel, what are the right specifications to aim for? EN590 (regular diesel) or EN15940: 2016 Class A (HVO-100)? These choices are critical because they have a direct bearing on process design and the choice of catalyst technology.

Our research and development programs have been focused on refining HydroFlex™ technologies for more than a decade. Based on extensive knowhow from processing fossil-based feedstocks, the research has also encompassed valuable experience from early commercial units[11] – both in co-processing or stand-alone modes.

As the name suggest, HydroFlex™ technology is flexible. Several layouts are possible, and choosing the right one depends on the nature of the feedstock along with the properties of the end product.

Sour mode
This layout is the right choice if you are aiming to produce renewable diesel from feedstock consisting of triglycerides. The sour mode layout has a CAPEX up to 35% lower than the more flexible sweet mode. Figure 3 shows a simplified flowsheet of the layout.

Sweet mode
A range of designs and layouts are possible. The layout shown in Figure 4 enables a large degree of flexibility, so you can produce renewable jet fuel and diesel from a wide variety of feedstocks.

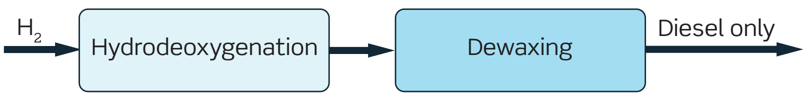

Figure 3. Simplified flow sheet of sour mode HydroFlex™

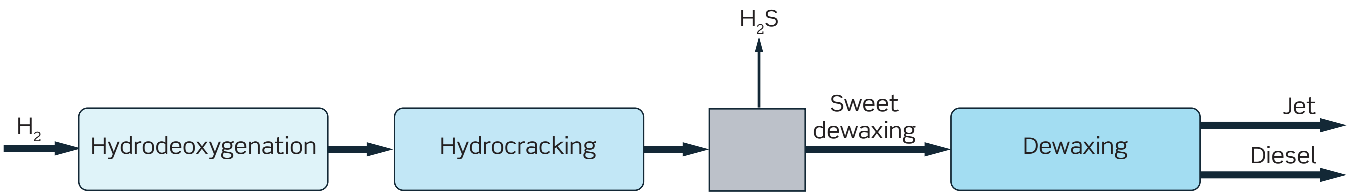

Figure 4. Simplified flow sheet of sweet mode HydroFlex™.

Catalyst technology

Transforming each renewable feedstock into a particular type of transport fuel demands the application of specific catalysts. For example, thoroughly designed guard beds are required to handle the high levels of contaminants such as phosphorus, sodium, and silicon present in some renewable feedstocks.

Selecting the right hydrotreating catalyst is critical for choosing the optimal reaction pathway (HDO vs. decarboxylation) as the catalyst has a huge effect on the yield structure. We have developed a wide selection of hydroconversion catalysts, shown in Table 3, in order to optimize yield structure and cycle length.

TABLE 3
Topsoe hydroconversion catalysts for renewable feedstocks.

Catalyst	Oyxgen removal	S removal	N removal
TK-335	++	+	+
TK-337	+++	++	++
TK-339	++	+	+
TK-340	+++ (hydroconversion)	+	+
TK-341	+++	++	++
TK-359	++++	+++	+++

As mentioned above, hydrotreating triglycerides produces normal parraffins. As these molecules dictate the cold flow properties of the resulting diesel, dewaxing might be needed. As shown in Table 4, we offer a wide range of dewaxing catalyst technologies for both sweet and sour modes. Each catalyst has a particular attribute, such as high yield, high tolerance to silicon and nitrogen or effective end-point reduction. Factors such as the type of feedstock, the specifications of the end product, and the unit layout, all play an important role in selecting the right combination of catalyst technologies.

TABLE 4
Overview of Topsoe's dewaxing catalysts.

Name	Metals	Zeolite	Reaction pathway	Mode	Special capabilities
TK-920 D-wax™	Noble	3	Isomerization	Sweet	High yield and high activity
TK-930 D-wax™	Base metals	3	Isomerization	Sour	High yield with high tolerance to S and N
TK-935	Base metals	2	Selective cracking of normal paraffins	Sour	High activity with high tolerance to S and N
TK-928	Base metals	1	Isomerization and cracking	Sour	Specially designed for use with renewable feedstocks
TK-932	Base metals	1	Isomerization and cracking	Sour	End point reduction and volume swell

Summary & conclusions

In many countries, legislation is driving the move towards producing transport fuels from renewable feedstocks. This is creating opportunities for refineries to increase their market share. As a result, current development in the field is extremely fast.

From simple triglycerides to complex pyrolysis oils, renewable feedstocks vary considerably in terms of their properties, level of contamination and availablilty. And from renewable diesel to jet fuel, there is also considerable variation in the properties, specifications and application of the end product.

Because of this, refineries need a flexible solution. And that comes down to choosing the right process design and catalyst technologies.

References

[1] Technology Roadmap, Delivering Sustainable Energy, International Energy Agency, http://www.iea.org/publications/freepublications/publication/Technology_Roadmap_Delivering_Sustainable_Bioenergy.pdf; 2017

[2] Peña, N., Biofuels for Transportation: A Climate Perspective, http://www.c2es.org/publications/biofuels-transportation-climate-perspective; 2008

[3] Donnis B., Egeberg R.G., Blom P., Knudsen K.G., Hydroprocessing of bio-oils and oxygenates to hydrocarbons. Understanding the reaction routes, Topics in Catalysis (2009), 52, 229-240

[4)] World Energy Outlook 2016, https://www.iea.org/Textbase/npsum/WEO2016SUM.pdf

[5] Official version of the compromise text agreed in the trilogue for the new EU renewable energy directive 2021-2030: http://data.consilium.europa.eu/doc/document/ST-10308-2018-INIT/en/pdf

[6] Mante O.D., Dayton D.C., Gabrielsen J., Ammitzboll N.L., Barbee D., Verdier S., Wang K., Integration of catalytic fast pyrolysis and Hydroprocessing: a pathway to refinery intermediates and "drop-in" fuels from biomass, Green Chemistry (2016), 18, 6123-6135

[7] Dabros T.M.H., Stummann M.Z., Høj M., Arendt Jensen P., Grunwaldt J.D., Gabrielsen J., Mortensen P.M., Degn Jensen A., Transportation fuels from biomass fast pyrolysis, catalytic hydrodeoxygenation, and catalytic fast hydropyrolysis, Progress in Energy and Combustion Science (2018), 68, 268-309

[8] News from Biofuels Digest:
https://www.biofuelsdigest.com/bdigest/2016/07/04/canfor-to-invest-70-million-in-400000-bpy-licella-biocrude-plant/
https://www.biofuelsdigest.com/bdigest/2018/01/14/steeper-energy-in-licensing-deal-with-silva-green-fuel-advanced-biofuel-project/

[9] Al-Sabawi M., Chen J., Hydroprocessing of biomass-derived oils and their blends with petroleum feedstocks: a review, Energ. Fuel. (2012), 26, 5373-5399

[10] Verdier S., Wiwel P., Gabrielsen J., Frøsig Østergaard L., Qualitative Round Robin Study – Analyses of Renewable Feedstocks, Topsoe Technical Paper (2018)

[11] Egeberg R., Knudsen K., Nyström S-, Lind Greenfelt E., Efraimsson K., Industrial-scale production of renewable diesel, Petroleum Technology Quarterly (2011), 16 (3)

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