

Hydroprocessing
White paper

HYDROPROCESSING OF RENEWABLE FEEDSTOCKS – CHALLENGES AND SOLUTIONS

TOPSOE

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Hydroprocessing of renewable feedstocks is an area that is developing very quickly in several regions, primarily in EU and USA, due to legislation requirements. Also preparing to adopt the latest technologies is India; by processing renewable feedstocks, India aims at reducing the CO_2 emissions and its dependency on fossil fuels.

Processing such feedstocks poses unique challenges:

- Corrosion issues due to the high TAN number and high Cl content
- High exothermic reactions and high hydrogen consumption
- Catalyst deactivation and pressure drop build-up due to the presence of contaminants, such as Si and P
- Impact on product properties, such as density and cold flow properties, that might require additional processing
- Obtaining reliable supply and proper quality of renewable feedstocks

These unique challenges require customized solutions to account for the specific needs of each refinery, the product quality, the nature of the feedstock, hydrogen availability, and integration with the existing refinery units.

For co-processing or processing a 100% renewable feedstock, Topsoe's solutions provide full feedstock flexibility and enable clients to produce clean fuels from a wide range of feeds, including vegetable oils, animal fats, used cooking oils, pyrolysis oils, residues from pulp mills, etc.

Compared to the processing of fossil fuels, the conversion of renewables to transport fuels poses new types of challenges: high level of contaminants (such as phosphorus), large exotherms, and corrosion due to oxygenated compounds. We have developed specific guard catalysts to handle these contaminants and ensure full cycle length. Since the cloud point of renewable fuels is higher than fossil fuels, dewaxing becomes extraordinarily important when producing diesel from renewable sources. Topsoe has developed a new generation of dewaxing catalysts that improve the cold flow properties of renewable fuels by selective isomerization, with minimum yield loss.

Based on our fundamental and applied R&D research, we have optimized our catalyst technology and process design, and, today, we are market leaders in providing solutions to hydroprocess renewable feedstocks.

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1. INTRODUCTION

In many countries, ambitious targets have been set to use renewable energy within the transport sector, as this sector is expected to experience a significant growth[1]. Various types of renewable feedstocks can be used to produce renewable transport fuels[2]:

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

The conversion processes to upgrade the afore-mentioned biomass types can be divided into three classes as shown in **Table 1**. Hydrotreating of fatty acids-based feedstocks, such as vegetable oils and animals fats, is well-understood[3], and these feedstocks are already hydrotreated in many refineries in the world, accounting for 4% of the global production of renewable transport fuel in 2016[4]. However, regulations are likely to limit the use of these types of feedstocks due to "food vs. fuel" and land use critical issues. For example, the so-called RED II legislation (Renewable Energy Directive for 2021-2030 in the EU) plans a phaseout of high-ILUC (Indirect Land Use Change) crop-based biomass (such as palm, soya, rapeseed, sugars, or cereals) by 2030. A limit of 1.7% will also be set for processing used cooking oils and animal fats[5]. Pyrolysis is believed to be a key process to produce biocrudes that can be further hydrotreated, especially catalytic fast pyrolysis[6] and catalytic fast hydropyrolysis[7]. Hydrothermal liquefaction is also another route, heavily studied to produce biocrudes, and demonstration units are under construction[8].

In India, renewable policies are alsobeing strengthened. In June 2018, the Indian government released the National Policy on Biofuels 2018[9].

The 2030 indicative targets were established as follows:

- 20% blending of ethanol with gasoline
- 5% blending of biodiesel with diesel

Use of indigenous feedstocks is also a high priority, especially non-edible oil seeds, used/waste cooking oils, animal tallow, acid oils, and algal feedstocks, among others. Currently, biodiesel is produced in six plants in India with a combined capacity of 650 million liters of biodiesel per year. At the moment, renewable diesel is not produced in India; however, research, development, and demonstration in the field of advanced conversion technologies are prioritized.

TABLE 1: Possible conversion steps to upgrade biomass intro transportation fuels[1, 2]

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

2. CHALLENGES OF HYDROTREATING RENEWABLE FEEDSTOCKS

Processing renewable feedstocks is challenging in many ways compared to processing fossilbased feedstocks. Some of these issues are listed below.

Corrosion:
Vegetable oils or tall oil may contain high amounts of free fatty acids which may cause severe corrosion of pipes, heat exchangers, reactors, and other equipment. Cl present in the feedstock will be converted into HCl in the hydrotreating reactor, which can cause corrosion in the reactor effluent stream and in the sour water. Carbonic acid is formed in the reactor effluent due to the presence of water and CO_2. It is therefore crucial to consider such parameters when studying processing of renewable feedstocks.

High hydrogen consumption:
Large amounts of hydrogen are required to upgrade renewable feedstocks (values of 300-400 Nm^3/m^3 are typical for 100% renewable feed). Therefore, higher make-up hydrogen and quench gas flows are needed, even when coprocessing small amounts.

Thus, it is crucial to check the refinery hydrogen balance, as the unit capacity may end up being lowered. The high hydrogen consumption results in a very high heat release in the reactor which needs to be accounted for in design.

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

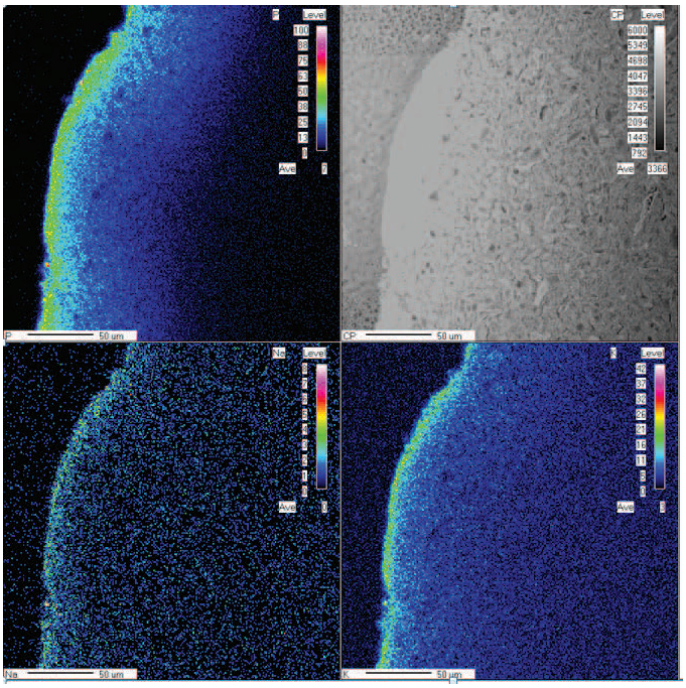
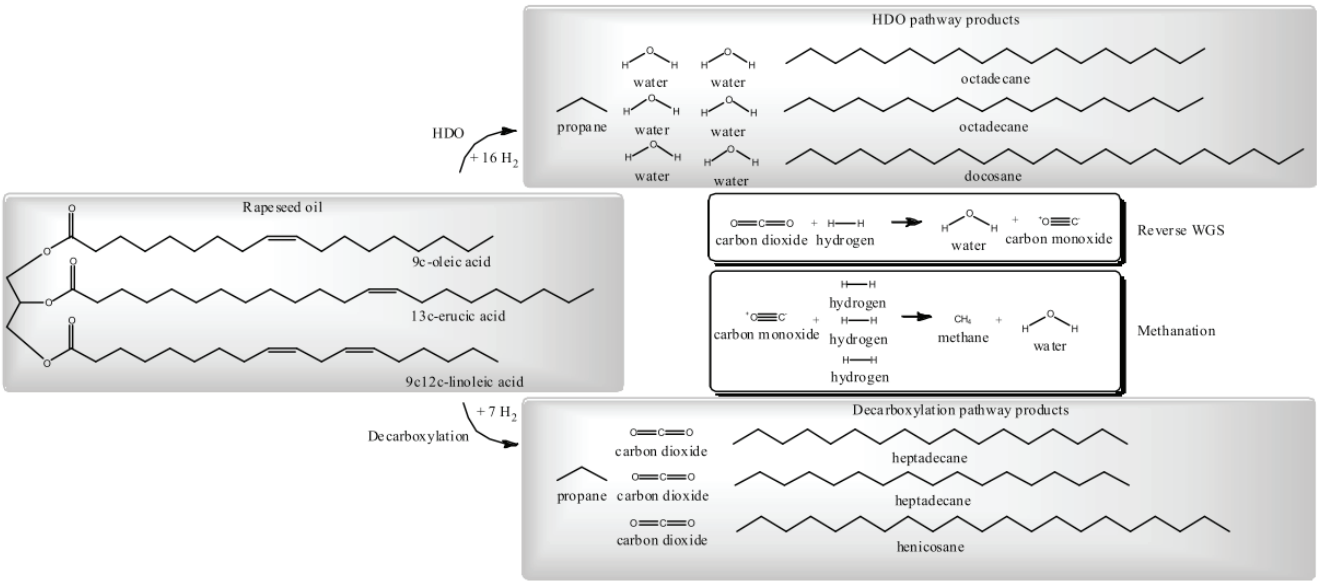


FIGURE 2: Reaction pathways in hydrotreating of rapeseed oil



Deactivation:
Contaminants in renewable feedstocks (such as P, alkali metals, and alkaline earth metals) are known to cause operating problems[11]. For example, build-up of phosphate deposits has been reported to cause pressure drops and fast catalyst deactivation. Furthermore, phosphorus may also coat the external surface of catalysts and prevent access to the pores, as shown in **Figure 1.** This is the reason why strict specifications are normally given for the concentrations of contaminants in the feedstock.

Analyses of contaminants:
Topsoe coordinated a qualitative round-robin study in 2018 between 12 laboratories. Three samples of renewable feedstocks were sent to the participants (vegetable oil, animal fat, pyrolysis oil), and a large number of analyses were conducted using international standards: elemental analysis (C, H, N, S, O), physico-chemical properties (SG, cloud point, pour point, TAN, water content), and contaminants (Al, Ca, Fe, K, Na, Mg, P, Si, Zn). Large deviations were observed, as shown in **Table 2**, especially for animal fat and pyrolysis oil.

Significant efforts should be dedicated to improve the reproducibility of analyses of renewable feedstocks.

Feed supply:
This topic is actually the main concern for many refiners who want to process renewable feedstocks. Does the potential supplier provide a reliable market knowledge (pricing, availability, diversity of the offer)? How stable is the quality of the feedstock? Is the feedstock available at all times and in a regular and reliable way? Will the feed be pretreated or does it need to be pretreated on site? Does the supplier provide a feedstock following the company's criteria for sustainability?

Product properties:
When triglycerides are hydrotreated, the products are mostly n-paraffins, as shown in **Figure 2**. This results in poor cold flow properties, and it should therefore be addressed, especially if artic diesel is required. 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.

3. HYDROFLEX™, A FLEXIBLE TECHNOLOGY FOR ALL TYPES OF FEEDSTOCKS AND PRODUCTS

Many factors have to be considered when preparing the process design and choosing the catalyst technology.

The first critical step is the choice of the desired product. Diesel or jet fuel? If one is considering diesel, which specifications should be targeted? EN590 (regular diesel) or EN15940:2016 Class A (HVO-100)? These choices are critical and will affect the process design and choice of catalyst thechnology.

Topsoe has been developing the HydroFlex™ technology for more than 10 years now based on the extensive know-how from processing fossil-based feedstocks. This has been done using dedicated R&D programs and experience from commercial units[13] - either in coprocessing mode or stand-alone.

Several layouts of the HydroFlex™ technology are possible, depending on the nature of the feedstock and on the desired product and its properties.

- Sour mode: this layout can be used if renewable diesel is the desired product and the feedstock consists of triglycerides. This layout has a lower CAPEX compared to the more flexible sweet mode. A simplified flowsheet is shown in **Figure 3**.
- Sweet mode: several designs are possible. The one showed in **Figure 4** allows a wide flexibility and enables production of renewable jet fuel and diesel and the use of a large selection of feedstocks.

FIGURE 3: Simplified flowsheet of the sour mode HydroFlex™

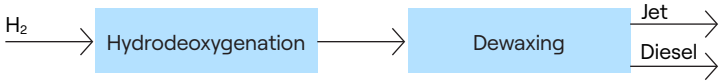
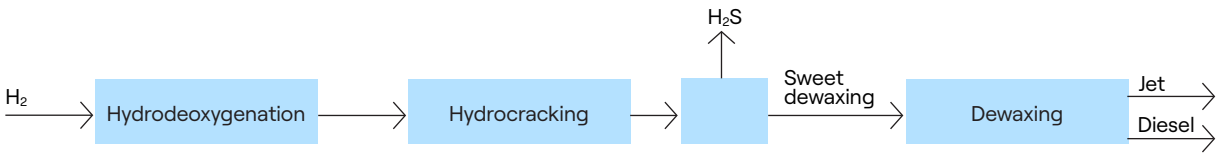


FIGURE 4: Simplified flowsheet of a sweet mode HydroFlex™



4.
CATALYST TECHNOLOGY

Specific catalysts have to be used when upgrading renewable feedstocks. For example, thoroughly designed guard beds have to be prepared in order to handle the high levels of contaminants, such as P, Na, and Si. The choice of hydrotreating catalyst is also critical when it comes to choosing the reaction pathway (HDO vs. decarboxylation), as it affects the yield structure. Topsoe developed a wide selection of hydroconversion catalysts, shown in **Table 3**, in order to optimize the yield structure and the cycle length.

TABLE 3. Topsoe's 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 previously mentioned, hydrotreating of triglycerides produces normal parraffins. As these molecules are controlling cold flow properties, dewaxing might be needed. Topsoe offers a large selection of dewaxing catalyst technologies (**Table 4**) in both sweet and sour modes with different capabilities: high yield, high tolerance to S and N, end point reduction, etc. Depending on the feed, the product specifications, and the unit layout, one of these catalyst technologies can be chosen.

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

5.
SUMMARY & CONCLUSIONS

Upgrading of renewable feedstocks to produce transport fuels is developing quickly due to legislation and economic incentives in many countries. In order to deal with a wide variety of feedstocks (from simple triglycerides to complex pyrolysis oils) and different product specifications for renewable diesel or jet fuel, the right process design and catalysts have to be chosen.

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Our mission is to combat climate change by helping our partners and customers achieve their decarbonization and emission-reduction targets, including those in challenging sectors: aviation, shipping, and production of crucial raw materials.

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