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SCIENCE BEHIND TECHNOLOGY

Requirements and solutions for the pre-treatment of HVO feedstocks

Hydrotreated vegetable oil (HVO) can reduce the use of fossil fuels and recycle waste streams but its production requires efficient, flexible, safe, reliable and sustainable pre-treatment of feedstocks.

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To address global warming challenges, it is essential to reduce the use of fossil fuels, which is the objective of the European Commission's 'Fit to 55' and Renewable Energy Directive (RED) II policies. The EU aims to reduce net greenhouse gas emissions by at least 55% by 2030 compared to 1990 levels and to define a common framework for the promotion of renewable energies. Hydrotreated vegetable oil (HVO) also called hydro-processed esters and fatty acids (HEFA) is a renewable diesel that can reduce fossil fuel use and recycle waste streams. European demand for drop-in biofuels – HVO and sustainable aviation fuel (SAF) – will significantly increase in the coming years, supported by higher blending targets and the introduction of new mandates for the aviation sector. It is projected that the HVO/HEFA share in European oil-based biofuel demand will increase to 35% by 2030.

Biodiesel, HVO and SAF

Conventional (first generation) biodiesel is a diesel fuel consisting of long-chain fatty acid methyl esters (FAME) typically made by transesterification of vegetable oils or animal fats. Biodiesel has to meet international quality standards such as the ASTM D6751 or EN14214 and is approved for blending with petroleum diesel.

Renewable diesel is a biomass-derived fuel suitable for use in diesel engines and meets the ASTM D975 or EN15940 standards for synthetic diesel. It consists of hydrocarbons and is mostly produced by a hydrotreating process but it can also be obtained via gasification, pyrolysis or other bio- and thermochemical technologies. The term HVO is used for renewable diesel fuels produced via a so-called hydrotreating process (hydrogenation and hydrocracking) of different feedstocks, such as vegetable oils, waste cooking oils, animal fats, acid oils and fatty acid distillates.

HVO, also called green diesel, has similar properties as fossil diesel but with some differences such as a lower density and higher energy content. It typically has a low sulphur content, is free from oxygen and aromatic hydrocarbons, and has a high cetane number.

HVO offers a series of benefits over FAME, such as reduced nitrogen oxide (NOx) and particulate emissions, better storage stability and better cold flow properties. It can be used in existing diesel engines without blending limitations. SAF is the commonly used term for nonpetroleum synthesized jet fuel components produced accordance with ASTM D7566 specifications. It is derived from renewable resources that enable a reduction in net life cycle carbon dioxide emissions compared to conventional jet fuels. SAF can be produced from waste and plant-based raw materials using essentially the same technology as for HVO production. When SAF is blended with conventional jet fuel, it meets ASTM D1655 specifications. All major European and US airlines have recently announced that they will start using increasing volumes of SAF voluntarily in anticipation of a future compulsory SAF proportion.

HVO Technology

The EU's REDII promotes the use of biofuels, favouring next-generation biofuels that are obtained from non-food waste feedstocks. Today, the only commercial alternative to FAME is HVO which can be obtained from waste feedstocks, while awaiting larger quantities of raw lignocellulosic and algal biomass.

The HVO process uses hydrogen, instead of methanol, in the conventional biodiesel process. Bio-propane is the major by-product and there is no low-value glycerol production. HVO can be blended with fossil fuel in higher ratios than the 7% used nowadays for biodiesel. The same feedstocks can be used for HVO and biodiesel production. However, the technology and the final products are different and producers have a different core activity. While biodiesel is mainly produced by food oil refiners, HVO production is mostly carried out by petrochemical companies because they are familiar with the hydrotreatment process, which typically

operates in two stages. The double bonds of the hydrocarbon chains are first saturated with hydrogen. This is followed by the elimination of oxygen atoms through three parallel mechanisms: hydro-deoxygenation, decarboxylation and decarbonylation. An extra step is mandatory for SAF production. Catalytic hydrotreatment is carried out at a high temperature (from 300-400°C) and hydrogen pressure (between 3-20 MPa). Sulphide nickel-molybdenum (Ni-Mo) and cobalt-molybdenum (Co-Mo) supported on alumina are the most common catalysts used, along with sulphur-free noble metals such as platinum (Pt) and palladium (Pd) or zeolite-supported Pt catalysts. Along with the process temperature and pressure, the catalyst type has an important impact on the final HVO product quality (compositional distribution).

HVO Markets and Producers

Today's main HVO markets are in Europe and the USA but new markets are developing fast in other continents as well. While biodiesel is still the most common biofuel in Southeast Asia, HVO production is also taking off in that region. Global HVO production capacity is expected to exceed 20M tonnes/year in the coming years.

Several companies have developed in-house HVO production processes but, in most cases, the HVO technology is offered by licensors. The Finnish company Neste Oil, a pioneer in HVO technology, is today the leading renewable diesel and jet fuel producer worldwide. Its NEXBTL technology can turn a wide range of renewable feedstocks into premium biofuels and other products. Neste Oil's first commercial-scale HVO plant was set up in 2007 at Porvoo, Finland. Today, it also has large capacity plants in Asia and Europe. When the scheduled expansion of these plants is realized by the end of 2023, Neste Oil will have a global HVO production capacity close to 4.5M tonnes/year, including 1.5M tonnes/year of SAF. HYDROFLEX is the technology supplied under license by Denmark's Haldor Topsøe which was developed in 2004 in anticipation of new market trends. HYDROFLEX units run alongside conventional petrochemical units all over the world with full flexibility, allowing the transformation of any renewable feedstock into drop-in, ultra-low sulphur gasoline, jet fuel or diesel. ENI (Italy) has developed the ECOFINING system in collaboration with Honeywell-UOP and, in 2013, started up a green refinery project based on the conversion of two existing hydro-desulphurisation units in Venice and Gela into hydro-treatment processes. Several other plants using the technology are in operation in the USA and Europe. The VEGAN HVO technology developed and licensed by France's Axens Group is a flexible solution for hydro-treating a wide range of lipids and producing low-density, high cetane renewable diesel as well as renewable sulphur-free jet fuel. This technology was originally developed by IFP Energies Nouvelles in the mid-2000s and is the result of Axens' wide experience in conventional hydro-processing technologies and catalysts, with more than 200 units licensed in the world.

Feedstock Selection

A wide variety of products containing triglycerides and/or fatty acids can be used in HVO production. These include vegetable oils, beef tallow, waste, or used cooking oils (UCOs). There is also increasing use of wastes or residues such as non-food grade vegetable oils, low quality animal fats, sludge palm oil mill effluents (POME), distillers' grains and solubles (DGS) corn oil, or refining byproducts such as acid oils from soapstock, oil recovered from bleaching earth, fatty acid distillates, distillation pitches and even non-glyceride feedstocks.

Due to sustainability but also for economic and political reasons, producers are increasingly looking for lower quality, waste and non-food alternative feedstocks. The quality parameters of some raw materials used for HVO are presented in Table 1.

Table 1: Quality parameters of different HVO feedstock

RAW MATERIAL	FFA %	P PPM	METALS PPM	N PPM	S PPM	CI (TOTAL) PPM	POLYETHYLENE PPM
Edible Vegetable Oils	< 3	50-250	100-300	30-200	2-20	< 5	-
Crude Palm Oils	< 6	15-30	20-60	10-20	< 10	< 15	-
Used Cooking Oils	1-10	< 20	< 50	5-15	10-100	20-100	0-200
Animal Fats	2-35	50-1000	200-2000	50-1500	20-200	50-500	0-1000
Acid Oils	50-60	50-1000	100-1000	50-250	20-100	< 25	-
Palm Fatty Acid Distillates	> 85	< 5	< 10	< 10	< 10	< 10	-

Feedstock Pre-treatment

The HVO process requires efficient, flexible, safe, reliable and sustainable pre-treatment of feedstocks. In general, pre-treatment is necessary to remove impurities such as phosphorous, metals, polyethylene, nitrogen, sulphur and chlorine-containing components that are naturally present in some raw materials.

Pre-treatment is a critical step in protecting HVO catalysts and increasing their life span and to avoid operational problems in the industrial installation.

The quality requirements for feedstocks at the inlet of the HVO unit are mostly set by the HVO technology providers and are generally quite stringent (*see Table 2*). An efficient and flexible pre-treatment process will determine if, or to what extent, a low-quality feedstock can be used; this will directly impact the viability of the HVO plant. Pre-treatment of good quality raw materials (vegetable oils, UCOs and high-grade animal fats) is quite straightforward and can be accomplished by a series of processes that are already known within the edible oil refining sector. The basic configuration of a standard HVO pretreatment plant (*see Figure 1a*) normally has two cleaning sections: an acid degumming section followed by a dry pretreatment/ bleaching section. Acid degumming with washing efficiently removes most impurities such as phospholipids, metals and mineral salts. Dry pre-treatment/bleaching, with activated bleaching earth or silica, achieves the required low levels of contaminants. Animal fats and some UCOs may nevertheless require an additional second bleaching step to remove polyethylene and plastic residues that can be present in these raw materials (*see Figure 1b*). For other low-quality feedstocks, some additional steps may be required before the standard pre-treatment process. This includes a pre-filtration step to remove high levels of solid impurities, polyethylene and some nitrogen components (for example, from protein) and/or a specific heat pre-treatment step to remove phosphor-containing components and metals from very low-quality animal fats (EU Category 1 and 2 animal by-products) and acid oils, as the basic pre-treatment plant configuration fails to remove these contaminants to low enough levels. Finally, an alternative pre-treatment process has been developed for very poor quality feedstocks like some acid oils, distillation pitches and trap grease. This process mostly consists of fat splitting followed by fatty acid distillation. The process is very efficient at treating feedstocks with extremely high loads of contaminants, but often has lower yields than a classic pre-treatment process and has much higher Capex and Opex costs. Its application has, until now, been limited to low-capacity plants with difficult feedstocks.

Table 2: Inlet product specifications for different HVO technology providers

COMPONENT	UNIT (MAX)	OFFICIAL METHODS	PROV. A	PROV. B	PROV. C	PROV. D
Free Fatty Acids	%	AOCS Ca 5a-40	5	20	20	95
Moisture content	ppm	ISO 8534:2017, AOCS Ca 2e-84	500	500	700	500
Insoluble Impurities	ppm	AOCS Ca 3a-46	500	500	100	500
Unsaponifiable	%	AOCS Ca 6a-40	N.S.	1	1	N.S.
Phosphorus	ppm	AOCS Ca 17-01	3	3	2	3
Metals (total*)	ppm	AOCS Ca 17-01, ASTM D5185	10	5	5	10
Nitrogen	ppm	ASTM D4629	50	350	100	350
Sulfur	ppm	ASTM D2622, ASTM D4294, ASTM D5453	100	250	30	100
Chlorine (total)	ppm	EN 14077, ASTM D7359	10	50	5	50
Polyethylene	ppm	AOCS Ca 16-75	50	50	50	50

N.S.: Not Specified; * Ca, Mg, Fe, Na, K, B, Si, Zn, Al

Figure 1a: Overview of the pre-treatment of various raw materials for HVO

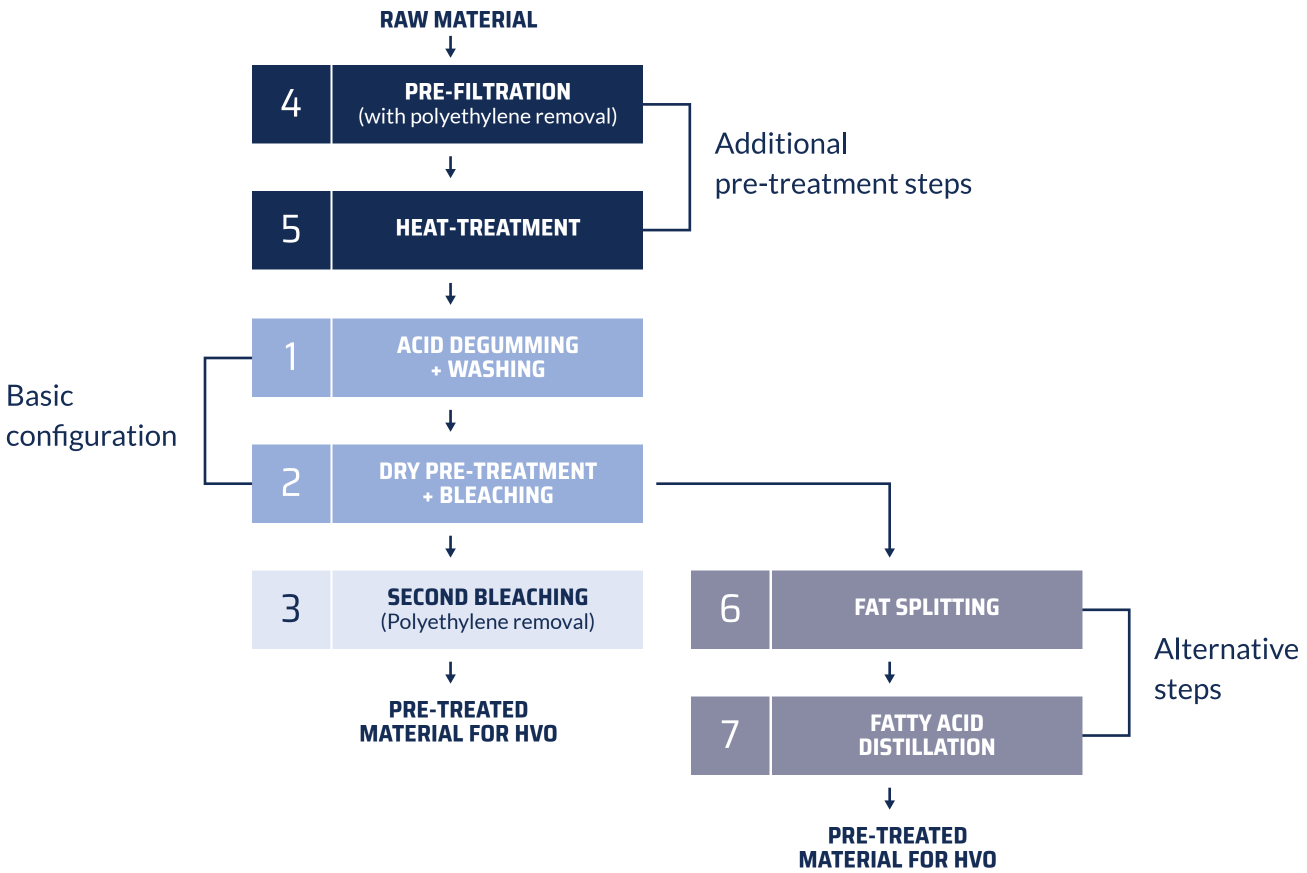

Figure 1b: Basic and alternative HVO feedstock pre-treatment processes

BASIC PROCESS	**WITH OR WITHOUT ADDITIONAL PRE-TREATMENT STEPS (3, 4 AND 5)**					
Edible Vegetable Oils			1	2		
Crude Palm Oils			(1)	2		
Used Cooking Oils			1	2	(3)	
Tallow Fats			(1)	2	(3)	
Animal Fats Cat. 3	(4)	(5)	1	2	3	
Fatty acid Distillates			(1)	2		
Animal Fats Cat. 1	4	5	1	2	(3)	
ALTERNATIVE PROCESS	**ADDITIONAL 6 AND 7 STEPS (NOT ALWAYS NECESSARY)**					
Acid Oils	(4)	(5)	(1)	(2)	6	7
Non-glyceride Feedstocks (Tall Oil, Distillation pitches ...)	(4)	(5)	(1)	(2)	6	7

Pre-treatments between brackets can be optional depending on feedstock composition/quality

Pre-treatment Providers

Providers of pre-treatment processes for HVO mostly originate from the vegetable oils and fats industries since the technologies are very similar to vegetable oil refining for food applications. The companies generally have an extensive portfolio of similar technologies. However, since HVO producers are increasingly focusing on low-quality feedstocks, existing processes need to be adapted and optimized to clean these feedstocks. In addition, as more pretreatment plants come into operation, greater operational experience is gained and this allows a continuous improvement in pre-treatment plant configurations to enhance efficiency, reliability and safety.

Desmet is one of the companies which supplies pre-treatment technology at the start of the HVO process to treat feedstocks. The objective is to guarantee the quality requirements set out by different HVO technology providers and to meet the high capacity ranges (up to 5,000 tonnes/day inlet capacity) required by this industry.

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