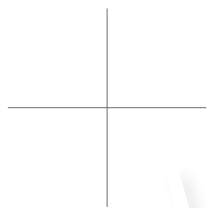


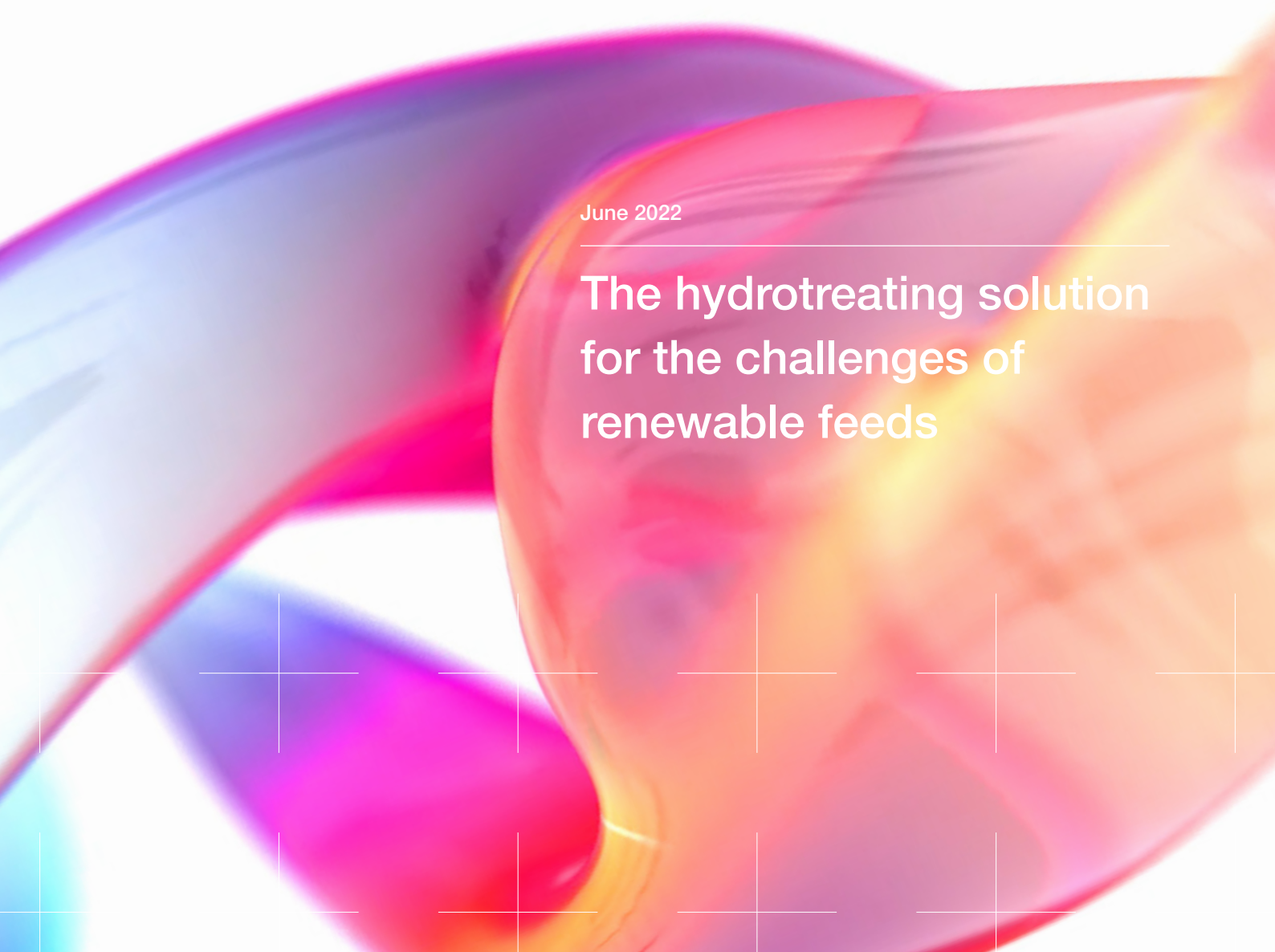
SULZER



White Paper

June 2022

The hydrotreating solution
for the challenges of
renewable feeds





The hydrotreating solution for the challenges of renewable feeds



The traditional oil & gas industry is transforming. Fossil fuels still dominate the energy landscape, but modern fuels are cleaner and more sustainable. Increasingly stringent regulations require a reduction in harmful emissions while boosting the volume of fuels from renewable sources into the finished products. Consumption of biomass-based fuels will continue to increase as more renewable mandates and clean fuel standards come into effect. At the same time, expanded processing capacity using innovative technologies will be necessary to sustain the drive towards a more environmentally conscious energy supply.

Author: [Matthew Clingerman Process Development Expert](#)

Renewable diesel, also referred to as hydrotreated vegetable oil (HVO), is a hydrocarbon fuel derived from biomass-based fats, oils, and greases (FOGs). It is materially different from biodiesel as shown in Figure 1. Various feedstocks are prepared from biomass using processes such as seed oil extraction, gasification, pyrolysis, and other biochemical and thermochemical technologies. Pretreatment of the resulting oil is required to purify the biomass prior to conversion into fuels. This step removes contaminants harmful to downstream catalysts and equipment. Once pretreated, hydroprocessing is used to convert the FOGs into renewable diesel. The resulting product meets ASTM D975 specifications for Tier III diesel in the USA and EN 590 in Europe as a drop-in fuel, indistinguishable from petroleum diesel. Alternatively, biodiesel is a mono-alkyl ester produced via transesterification. Here, the same biomass-based feedstocks are instead reacted with methanol to form fatty acid methyl esters and glycerin. Biodiesel meets ASTM D6751 and is approved for blending with petroleum diesel up to certain limits.



Sustainable aviation fuel (SAF) is also derived from renewable resources and can be produced by several different approved pathways. One pathway to SAF is to produce hydrotreated esters and fatty acids (HEFA) from biomass feeds via hydroprocessing. Catalyst having a more severe cracking function can be utilized to shift the yield from diesel range material into jet fuel. SAF is produced to the specifications defined in ASTM D7566 [1], and when blended into petroleum jet fuel meets D1655, allowing it to be used in existing aircraft and infrastructure. Previously, the EU had not considered SAF or alternative jet fuels (AJF) in the Renewable Energy Directive (RED), but a provision has been added in RED II [2].

Renewable diesel feedstocks

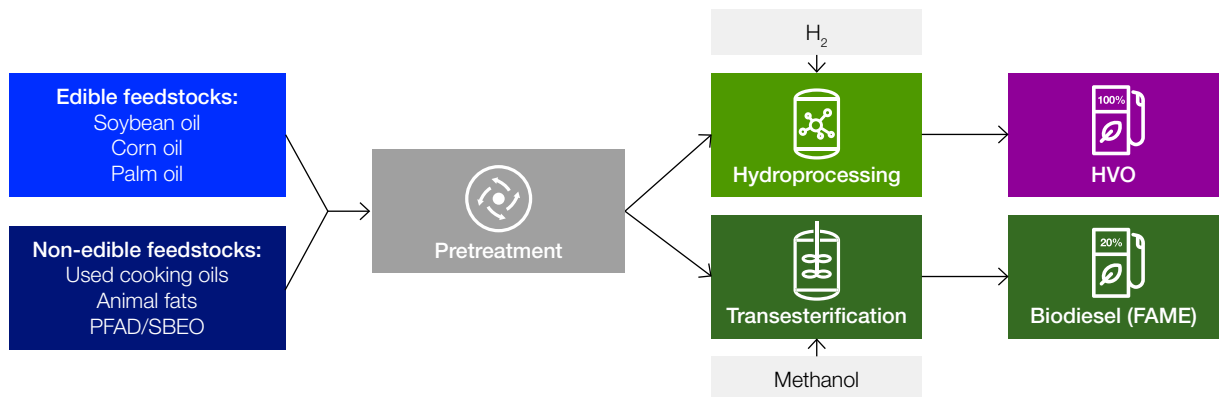
There are many feedstocks from which renewable diesel can be produced. Vegetable oils, seed oils, and rendered animal fats are the primary sources used today. Solid biomass, such as wood waste, can be used after conversion through pyrolysis or liquefaction processes. Other waste feedstocks are often used as well, including used cooking oil and yellow grease.

Most high purity fats and oils, including edible tallow, lard, and refined vegetable oils, are vital components in the global food chain and command premium prices. Technical grade fats and oils, including bleachable, white grease,

and once-refined soybean oil, are used in livestock and industrial applications as well as renewable fuels production. Lower quality fats and oils, including yellow grease and used cooking oils, may contain elevated concentrations of degradation products such as free fatty acids. These free fatty acids typically are not a problem for renewable diesel production because they are more easily converted into a paraffinic, diesel-range material. The availability and price of these materials might make them attractive as renewable diesel feedstocks compared to virgin vegetable oils, where hydroprocessing is an ideal upgrading technology.

Furthermore, feedstock usage varies widely by region. For example, rapeseed oil is the most common feedstock in Europe. Palm oil or palm fatty acid distillate is used for biodiesel production in Asia, although concerns of sustainability are raising questions about long-term usage as a feed for renewable fuels. In the US, the primary feedstocks for renewable diesel have been distillers corn oil, soybean oil, and tallow. Globally, used cooking oil has fast become a feedstock of choice originally due to its low cost and favorable economics. However, this has shifted as HVO producers moved quickly to secure a reliable supply, which increased prices significantly due to lower availability. Regardless, feedstock selection will continue to strongly influence the economics of renewable diesel production and is often the most critical factor determining the financial viability of a project.

Figure 1. Two pathways for biomass-based feeds: hydrotreating and transesterification



Reaction mechanisms

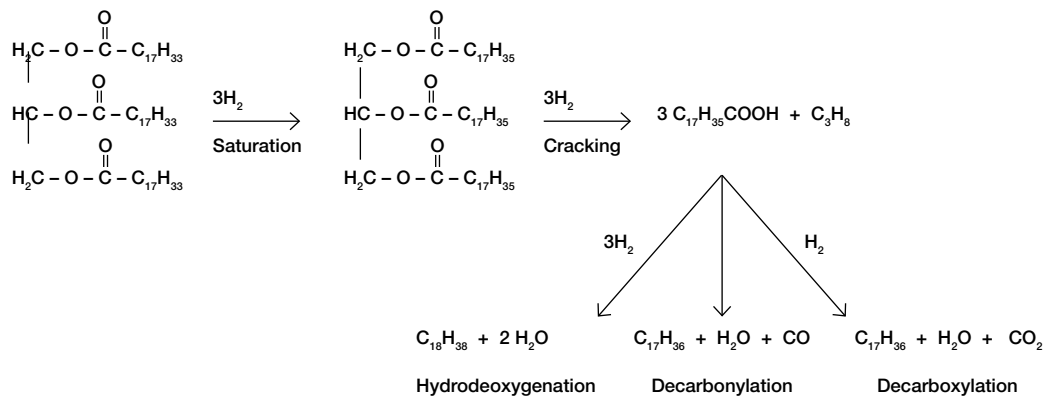
Figure 2 summarizes the reaction pathways typically observed. Triglycerides are converted into high cetane hydrocarbons at elevated temperatures and pressures over a bifunctional catalyst, e.g., NiMo/ γ -Al₂O₃. Reactor operating temperatures and pressures are set set >250°C and at or above 60 bar-g, respectively. Reaction products are formed either by hydrodeoxygenation (HDO), decarboxylation, or decarbonylation. The preference is towards HDO, since this reaction mechanism eliminates oxygen by reacting triglycerides and free fatty acids with hydrogen to form water and n-paraffins. Decarboxylation or decarbonylation eliminates oxygen to form carbon dioxide or carbon monoxide and n-paraffins. It also reduces by one carbon the length of the finished product. The HDO effluent can then be routed through various reaction steps depending on the desire final product. In most cases, a hydroisomerization step is used to improve the cold flow properties of paraffinic product from the deoxygenation step. Catalyst selection and reaction conditions can shift both the reaction mechanism described above as well as the overall yields towards lighter hydrocarbons, such as propane, jet, and gasoline range material.

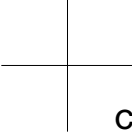
Benefits of renewable diesel

The benefits of renewable diesel have been well-publicized throughout the market. In short, these benefits include:

- > **Compatibility with existing engine and infrastructure:** renewable diesel is chemically identical to petroleum diesel, and therefore the existing infrastructure and engines can accept these fuels without blending limits. Biodiesel is limited in most applications as per ASTM D975.
- > **Lower greenhouse gas (GHG) emissions:** when compared to petroleum diesel, the EPA reports 64% reduction in lifecycle greenhouse gas emissions for biofuels produced from distillers sorghum oil [3].
- > **Flexibility:** renewable fuels are replacements for conventional diesel, allowing for multiple products from various feedstocks and production technologies that do not interrupt global food supply chains.

Figure 2. Reaction pathways in renewable diesel production





Challenges in renewable diesel hydroprocessing

When hydroprocessing petroleum-based feedstocks, the conventional two-phase, trickle-bed design transfers hydrogen from a vapor phase into the hydrocarbon liquid phase where it will be available to react with the hydrocarbon at the surface of the catalyst. This is accomplished by circulating very large volumes of hydrogen gas and the hydrocarbon through a catalyst bed. As the feed and hydrogen flow through the catalyst, hydrogen is absorbed into a thin film of oil that is distributed over the surface of the catalyst. Because the required amount of hydrogen can be large, the reactors are very large and operate under severe conditions. Large compressors also are used to circulate the hydrogen. These compressors are not only expensive, but also are high consumers of electricity.

One of the biggest operational challenges in hydroprocessing is catalyst coking. Coking occurs when hydrocarbon molecules become too hot in a hydrogen-starved environment. In this scenario, the hydrocarbon molecules crack to the point where coke is formed on the surface of the catalyst, leading to deactivation of the catalyst. This is often worsened by the difficulty controlling the temperature in conventional systems. Reactor inlet temperature can be readily controlled using the feed furnace and bypasses around the preheat exchangers. However, once the feed/hydrogen mixture is inside the reaction zone, the temperature of the oil/hydrogen mixture can only be adjusted by an outside source such as hydrogen quench.

These complications are exacerbated further when processing biomass-based feeds. Most renewable feedstocks derived from biological sources are highly olefinic and/or contain high levels of heteroatom contaminants. To produce a valuable product from such highly olefinic and highly contaminated feedstocks, a larger amount of hydrogen is required, typically between 1700-2500 scf/bbl, which is two to three times higher than conventional petroleum hydrotreating. Furthermore, these reactions are highly exothermic, generating significantly more heat than typical hydroprocessing of petroleum products. Typical exotherms are upwards of 200°C and require excess quench or hybrid reactor designs capable of removing high amounts of this excess heat.

The heat generated while hydrotreating biomass not only increases the likelihood of catalyst coking and deactivation, but also runaway reactions. A runaway reaction generates so much heat that the process can no longer be brought under control; despite cutting off heaters and maximizing cooling, a runaway reaction can continue to heat and has the potential to cause serious damage to the reactor and process equipment and endanger workers. This means that temperature control is even more crucial in a hydrotreating unit producing renewable diesel.

The composition of FOGs mean that pretreatment is required upstream of a hydroprocessing unit to remove contaminants that can negatively influence downstream operations. Common issues caused by contaminants such as phosphorus and chlorides include coking and plugging of the catalyst bed, corrosion, and high pressure drop. In addition to potential throughput limitations, it is also likely that desired product properties cannot be achieved due to issues caused by feedstock contaminants. Multiple processes exist for feedstock purification, including physical & chemical refining, hydrolysis, and thermal cracking, but it is crucial that the feedstock contaminants and reaction byproducts be controlled to prevent operational challenges within the hydroprocessing unit.

BioFlux® hydrotreating

BioFlux® hydroprocessing technology was developed to offer superior performance and overcome the challenges of renewable diesel production. The functional design aspects of BioFlux® also address issues caused by high exotherm common in biomass hydrotreating. Some of the advantages include:

- > Higher diesel yield
- > Efficient hydrogen management
- > Lower propensity for coking and over-cracking
- > Lower capital and operating expense
- > Reduced carbon footprint

A standard configuration for a BioFlux® Hydrotreating Unit is shown in Figure 3. BioFlux® hydrotreating reactors are based on MaxFlux® technology. Used for petroleum feedstocks, MaxFlux® overcomes the key deficiencies of the trickle-bed design described above by completely dissolving hydrogen into the liquid. The reactor design maximizes volumetric flux and the proprietary reactor internals ensure that the feed and hydrogen are completely mixed and evenly distributed for complete catalyst wetting.

The combined feed and hydrogen are fed to a downflow, fixed bed reactor loaded with hydroprocessing catalyst. In the first stage, the feedstock is reacted with hydrogen to saturate olefins and then remove oxygen. This produces a paraffinic hydrocarbon in the diesel boiling range through

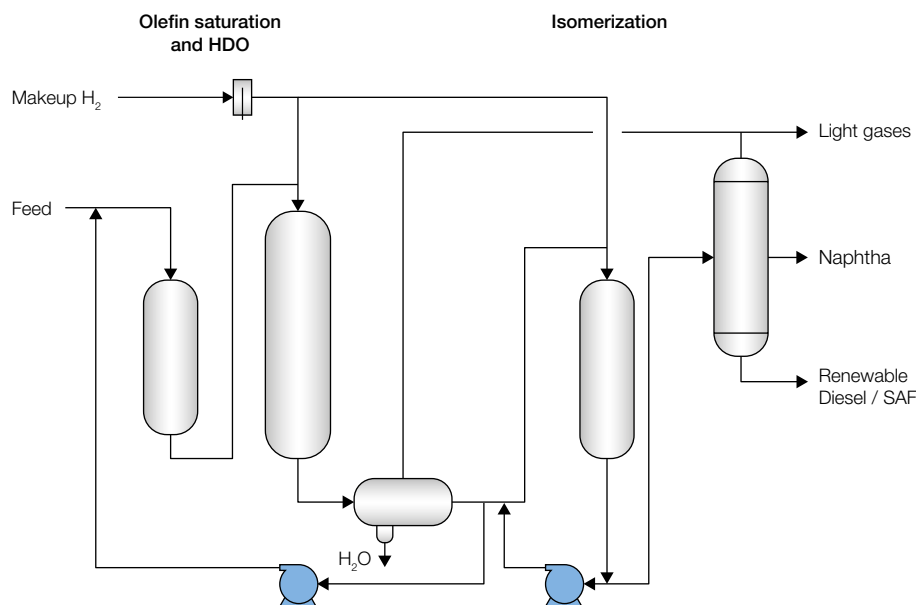
the reaction pathways described above. Water, CO₂, and other byproducts are also generated. These are removed from the reactor product, a portion of which is recycled to be mixed with the fresh feed.

The recycled effluent serves two primary functions. First, it provides pre-heat to the fresh feed. This reduces the need for supplementary preheat and lowers operating expense. Second, hydrogen can be dissolved into this stream that contains already-reacted molecules, which helps to increase the amount of hydrogen available for reaction. This reduces the size of the reactors required, lowering the capital expense.

The reactor vessel itself will be comprised of multiple reactor beds, the number and size of which depend on various factors, such as hydrogen consumption, to ensure sufficient conversion. Additional hydrogen is added in between beds, not as a quench, but as a make-up to re-saturate the feed and maximize availability for the reactions.

The product from the HDO reactor will meet most of the diesel specifications, such as cetane and density, but further processing in a hydroisomerization reactor may be required to improve cold flow properties. A similar multi-bed reactor design with isomerization catalyst and reactor effluent recycle is used to treat the HDO reactor product. Catalyst with additional cracking function may be used to produce renewable jet / sustainable aviation fuel.

Figure 3. BioFlux® renewable diesel process diagram





The advantages of BioFlux® technology

The high volumetric flux in the BioFlux® reactor allows it to operate as a heat sink, which stabilizes the temperature in the reaction zone. Liquids have higher heat capacities than gases and absorb heat more efficiently from its surroundings without a significant rise in temperature. By absorbing excess heat, the temperature throughout the reactor is equalized, which greatly reduces the formation of hot spots, and the subsequent coke formation, within the catalyst bed. This increases catalyst life and reduces operation and maintenance costs. Additionally, with BioFlux®, a runaway reaction is not possible since the amount of hydrogen contained in the reactor and recycle cannot support a runaway.

Additionally, hydrogen within the unit is managed in a more efficient manner. In a trickle-bed reaction system, the amount of hydrogen is typically much greater than the amount required for the reaction, which itself is often greater than the solubility of hydrogen in the feed. Thus, the reactions are diffusion-limited and require excess recycle hydrogen in order to maximize hydrogen partial pressure. The internals within a BioFlux® reactor completely dissolve the hydrogen into the feed such that the flow through the reactor is now in a single liquid phase.

The lower temperature rise also helps minimize over-cracking and undesirable side reactions. Reaction byproducts, namely light end hydrocarbons, are an undesirable product that must be recovered or treated at additional expense. Generation of these light ends increases with temperature rise. In conventional hydroprocessing, the problem of light ends production is further compounded by the tendency for a reactor to develop hot spots. Using liquid phase hydroprocessing, cracking is greatly reduced and thus the formation of undesirable byproducts is also lowered.

As described previously, in a renewable feedstock such as vegetable oil, the oxygen in the feed is partially converted into water. The greater the quantity of water produced, the more likely it is that two distinct liquid phases will form inside the reaction zone: a hydrocarbon phase and an aqueous phase. To maintain catalyst activity, the water created during the reaction between hydrogen and oxygen must be held in solution with the hydrocarbon. While the liquid recycle stream added to the feed provides a greater capacity for holding hydrogen in solution, it also increases the capacity for holding water in solution without creating an aqueous phase. Reaction conditions, such as temperature and hydrogen partial pressure, are also set to maximize target product yields and minimize byproduct formation. Prior to recycle, the water and other byproducts are removed from the reactor effluent to avoid build-up of these contaminants to a level above which damage to the catalyst would occur.



BioFlux® product yields

The yields from BioFlux® on a weight percentage basis are shown in Table 1. On a volume basis, it is nearly an even ratio, i.e., one barrel of renewable diesel can be produced from each barrel of feed. There is some variation depending on feedstock quality, but in general the process has a higher yield of diesel than other renewable diesel production processes.

The properties of renewable diesel from BioFlux® are compared to three different diesel specifications in Table 2: ASTM D975 (US), EN590 and EN15940 (Euro). ASTM D975 is the US standard for various types of diesel engines. There are seven different grades in this standard and BioFlux® Renewable Diesel meets the No 2 Grade and can be used interchangeably. EN15940 is the European standard for paraffinic diesel fuels. Vehicle manufacturers will validate use of these fuels in the engines they supply, as EN15940 have different ranges than standard diesel (EN590), such as a lower density. However, as a blending component, BioFlux® renewable diesel also meets the specifications according to EN590.

An integrated solution

The off gas generated from the BioFlux® hydrotreating unit is not only rich in hydrogen, but also in light hydrocarbons that can be used to generate additional hydrogen. Hydrogen is produced by catalytic reforming of the off gas and supplemental natural gas. The integrated steam methane reformer (SMR) is shown in Figure 4. Off gas is first passed through a membrane unit. From the membrane separation, the hydrocarbon-rich stream is fed to the feed treatment section of the SMR, while the hydrogen-rich stream is sent directly to the pressure swing absorption (PSA) section of the plant. This configuration is a means by which unreacted hydrogen can be recycled to hydrotreating unit. Moreover, using the off gases generated from renewable sources reduces the overall carbon intensity of the process. Natural gas feedstock to the SMR is displaced by a renewable source: the off gas from hydrotreated FOG. Naphtha, if produced in appreciable quantities, can also be used to generate hydrogen. If produced in sufficient quantities, the off gas and naphtha could eliminate the need for supplemental natural gas.

Table 1. Summary of yields from BioFlux® hydrotreating

	Maximum diesel case	Maximum SAF case
	Weight %	Weight %
Feed		
Vegetable oil	100	100
Hydrogen	2 – 4	2 – 5
Products		
Off gas	1 – 3	1 – 3
Naphtha	0 – 2	16 – 20
SAF	0	66 – 70
Diesel	83 – 86	0

Figure 4. Integrated hydrogen production

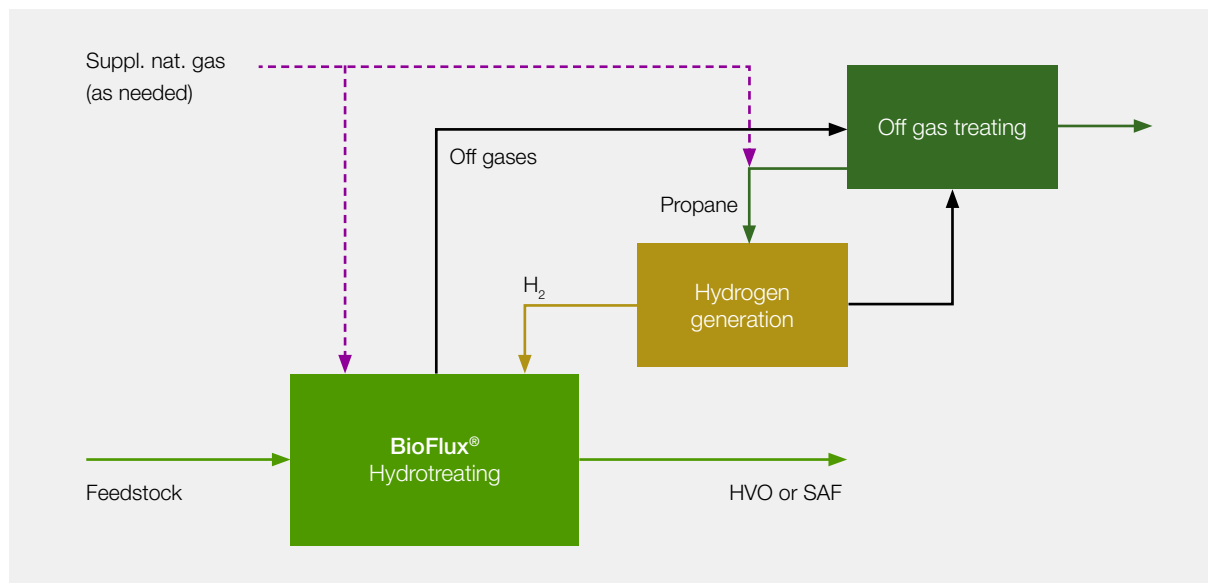


Table 2. Properties of BioFlux® diesel in relation to US and European specifications

	BioFlux®	ASTM D975	EN590	EN15940
Spec Gravity	0.76 – 0.80	--	0.820 – 0.845	0.765 – 0.800
Sulfur, ppm	< 1	≤ 15	< 10	< 5
Cloud Point, °C	To Spec	--	to -34	to -34
Cetane	> 70	≥ 40	51	> 70
FAME Content, %	To Spec	≤ 5.0	≤ 7.0	≤ 7.0
Flash Point, °C	To Spec	> 52	> 55	> 55
Water, wppm	To Spec	< 0.05 (vol%)	≤ 200	≤ 200
Cu Corrosion	Class 1 / 3	Class 3	Class 1	Class 1



A reduced carbon footprint

As stated above, renewable diesel produced from FOGs produce lower GHG emissions as compared to petroleum diesel. Recent advancements in HVO technology have led to a reduction in GHGs by up to 90% depending on the source of the raw material, the process by which the fuel is made, and the ultimate end use. Life cycle analysis (LCA) is the primary means by which CO₂ emissions from fuel production pathways are evaluated and compared. Carbon intensity (CI) is the grams of CO₂ equivalent per energy value of the fuel product, ie., gCO_{2-e}/MJ HVO. The CI of renewable diesel can be as low as 20 gCO_{2-e}/MJ or as high as 60. Higher carbon intensity fuels are the result of using feedstocks and processes that generate higher amounts of CO₂.

In the state of California, under the LCFS, producers are incentivized to reduce CI as much as possible, with a credit value that averages around \$160 / tonne of CO₂ reduction. Implementing BioFlux[®] helps producers reduce the CI of the finished fuels, thus ensuring that they will meet or exceed the CI reduction targets. With lower operating expense, longer catalyst life, and higher diesel yield, the CO_{2-e} per MJ of diesel is up to 25% lower than traditional hydrotreating technologies. Furthermore, by using the hydrotreater off gas to recycle and generate additional hydrogen, the CI from BioFlux can be reduced by further 3 numbers. All combined, for a 300 kta (~6'800 bpsd) unit, that could translate into a reduction in CO_{2-e} of up to 79'000 MT annually, for a value of nearly US\$12MM at \$160/MT.

Summary

Sulzer, a global leader in supplying state-of-the-art process equipment, is using their expertise to deliver world-class performance to renewable fuels producers worldwide. BioFlux[®] technology, developed by Duke Technologies and licensed by Sulzer GTC, is a low-CAPEX, low-OPEX solution for hydroprocessing of bio-based materials with higher levels of contaminants and olefins. By using a high liquid flux mode of operation, BioFlux[®] successfully manages reaction zone temperature and minimizes formation of reaction byproducts. This increases the yield of the higher valuable, drop-in renewable diesel product with lower hydrogen consumption and reduced carbon footprint. The process offers superior operational stability for extended catalyst life and is suitable for grassroots or revamp units, either standalone or in an integrated facility. To learn more about the BioFlux[®] technology and to receive a preliminary assessment of your feedstock, please contact us at www.sulzer.com.

BioFlux[®] is a registered trademark of Duke Technologies LLC.

For any inquiries please contact us:

Sulzer Chemtech
Neuwiesenstrasse 15
8401 Winterthur
Switzerland
Tel: +41 (52) 262 3722
sulzer.com

References

[1] ASTM International, D7566-20: Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, 2020.

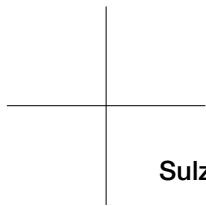
[2] Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources, 2018.

[3] Environmental Protection Agency, *Renewable Fuel Standard Program*, 2020.

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