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White Paper

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Pretreating renewable feeds to produce sustainable clean fuels

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Clean fuels from renewable sources are essential for meeting energy requirements of the future. New regulations and investment incentives continue to advance as demand for sustainable alternatives grows. Even as new facilities for producing renewable diesel and sustainable jet come online, low carbon fuels from biomass-based feedstocks are at the forefront of the fuels transition. As important as the finished product and feedstock, the conversion process from which these fuels are derived must also be sustainable, efficient, and flexible. BioFlux® Thermal Pretreat from Sulzer is the technology that unlocks maximum flexibility for converting fats to fuels.

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Understanding the Pathway

Many fats, oils, & greases (FOGs) from which Hydrotreated Esters and Fatty Acids (HEFA) and Hydrotreated Vegetable Oils (HVO) are produced share similar characteristics despite the source. They are primarily triglycerides, or three fatty acid chains on a glycerol backbone. They also contain varying amounts of free fatty acids (FFAs) in the oils. Of bigger concern, however, are the impurities present in the different FOGs, which can vary significantly. Some of the typical physical properties of these materials are shown in Table 1. These impurities are introduced into the oil not only in the processes that convert seed to oil, but also by nature itself. Waste oils, such as Used Cooking Oil (UCO) or Tallow, have additional impurities that increase the complexity of the treatment process.

Table 1. Typical ranges for various properties of FOGs

Property	UoM	Typical value
Free Fatty Acids	wt%	< 10
Moisture	wt%	< 0.5
Insoluble Impurities	wt%	< 0.5
Unsaponifiable Matter	wt%	< 0.5
Total MIU	wt%	< 3
Iodine Value	wppm	60 – 130
Total Metals	wppm	75 – 2’500
Phosphorus	wppm	5 – 275
Chlorides	wppm	20 – 2’000
Sulfur	wppm	0 – 50
Nitrogen	wppm	0 – 170

Fixed bed hydroprocessing is the most common means by which triglyceride or lipid-based feeds are converted into renewable fuels. Hydrotreating (HDT) of petroleum-based and bio-based feedstocks employs the same basic process: the addition of hydrogen for the removal of contaminants and converting the feedstock into a saleable fuel. As the use of renewable fuels accelerates, not only are new, dedicated facilities being constructed, but traditional petroleum hydrotreaters are being re-purposed by refiners making the switch to renewable feeds.

The critical first step in the process is the Pretreatment Unit (PTU). Upstream of the HDT, it removes the contaminants that can severely influence downstream operations and negatively impact product qualities. All of the impurities have some effect on yield, hydrogen consumption, or catalyst performance, but properties of particular concern in HDT processes include phosphorus, chlorides, total metals, and moisture content. Physical refining, which employs multiple steps for purifying the FOG, has been used for some time but was developed primarily for the edible fats and oils market. The process consists of acid degumming, mechanical separation, and bleaching, but additional steps and multiple units may be required as contaminant levels increase. Although generally capable of reaching low impurity levels, treatment to ultra-low levels of certain contaminants is generally not possible without significant additional investment. Other processes have been developed, but they use high pressure or introduce water into the system. In either process, though, the fatty acid chains remain unconverted.

When feeds pretreated via these methods are processed in a hydrotreater, olefin saturation, deoxygenation, and isomerization are still required. To produce a valuable product from such highly olefinic and highly oxygenated feedstocks, a large amount of hydrogen is required, typically >2,500 scf/bbl (> 410 Nm3/m3). This is up to 300% higher than typical petroleum hydrotreating. Furthermore, these reactions are highly exothermic, generating significantly more heat than typical hydroprocessing of petroleum products. All combined, these characteristics of FOGs lead to inefficient HDT operation and limit opportunities for co-processing and hydrotreater conversion.

A novel idea

BioFlux Thermal Pretreat is an alternative process designed to economically treat FOGs and enable more efficient hydrotreating operations. Biomass-based FOGs are converted using conventional refinery equipment and processes, which is more beneficial in several ways

- CAPEX and OPEX are lower
- No acid or caustic materials are used in the process
- No solid waste
- No mechanical separation (i.e., centrifugation)

The BioFlux Thermal Pretreat is a thermal cracking process that converts the FOGs in the PTU while impurities are removed. The steps of acid degumming, centrifugation, acidic or supercritical water washing found in other processes are not required in the BioFlux Thermal Pretreat process. Instead, material is heated to temperatures at which the triglyceride molecules are cracked into distillate range hydrocarbons that are a mixture of paraffins, olefins, and aromatics. Some of the feedstock remains unconverted but can be recycled to be cracked. The product properties and yield profile are determined by operating severity and internal recycle rate. As in the hydrotreating process, aqueous waste and off gas are generated from the process. Unlike other processes, glycerin, solid waste, or other unwanted byproducts are not produced in the BioFlux Thermal Pretreat. A comparison of the different processes is shown in Table 2.

Furthermore, the typical targets of FOG pretreatment – metals, phosphorus, and chlorides – are removed to levels at which the performance of the HDT unit will not be impacted. An example of the product properties is shown in Table 3. The process performance indicated here was achieved in a commercial plant that began operation in 2023. The ultra-low impurity levels reached in the commercial plant confirm the results obtained earlier in pilot plant studies.

Typical grassroots HEFA & HVO units consist of two stages: hydrodeoxygenation (HDO) followed by isomerization. As mentioned above, total hydrogen consumption is typically >2,500 scf/bbl (410 Nm3/m3). However, conversion of the FOGs in the BioFlux Thermal Pretreat unit can significantly reduce the hydrogen requirements in the HDT unit. By cracking the triglycerides and removing oxygen outside of the hydrotreater, both the hydrogen consumption and exotherm are significantly reduced. The BioFlux Thermal Pretreat unit can reduce hydrogen consumption in the HDT unit up to 60%. Not only are operating expenses due to hydrogen reduced, but this also will significantly reduce investment in the HDT.

These process efficiencies and benefits extend across all of the units in the HEFA/HVO biorefinery as summarized in Figure 1.

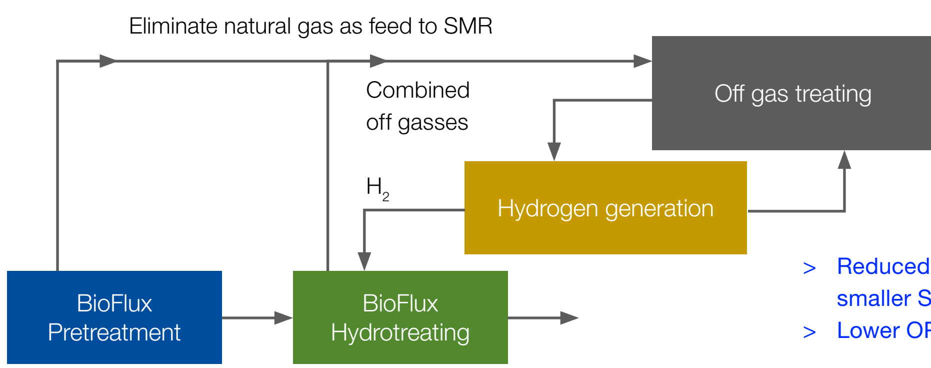
Table 2. Comparison of pretreatment processes

	Edible oil technology	Fat splitting	BioFlux Pretreatment
Process	Acid degumming, bleaching	Ultra-high pressure hydrolysis	Thermal Cracking
Primary Product(s)	Treated, unconverted FOGs	Fatty Acids	Distillate, Fuel gas
By-products	Effluent waste, spent sorbents	Glycerol	Water
Catalyst	None	Supercritical Water	None
Product Phosphorus	< 3 wppm	< 2 wppm	< 1 wppm
Product Chlorides	< 5 wppm	< 5 wppm	< 1 wppm
Total Investment Cost	2.3 x BASE	1.5 x BASE	BASE

Table 3. Pretreatment product properties from BioFlux Thermal pretreat

	Distillers Corn Oil		Soy		Used Cooking Oil	
	Feed	Product	Feed	Product	Feed	Product
Phosphorus, ppm	5	< 1	26	< 1	12	< 1
Chlorides, ppm	14	< 0.01	< 0.01	< 0.01	32	< 0.01
Total Metals, ppm	45	< 6	30	< 8	169	< 9

Figure 1. Summary of Benefits to Using BioFlux Thermal Pretreat



- Reduced CAPEX with smaller SMR
- Lower OPEX, less catalyst

- Reduced CAPEX
- No hazardous waste
- Simpler operation

- Reduced CAPEX by shrinking HDO reactor loop, eliminating OSR
- Lower OPEX by reducing recycle, smaller make-up compressor
- Less catalyst in HDO and potentially no precious metal in the Isom reactor
- May use a single reactor for max HVO case

Decarbonization with BioFlux Technology

The adoption of renewable feedstocks to produce fuels has been a major driver towards a more sustainable transportation industry. In the State of California, fuel producers and sellers are incentivized to produce a fuel that adheres to ever decreasing Carbon Intensity (CI) targets. In Europe, CO_2 emissions are taxed under a cap-and-trade scheme. Thus, selection of pretreatment, hydrotreating, and hydrogen generation technologies used in the biofuels refinery will have a direct impact on the facility's economics.

Improving CI for only the biorefinery portion of the well-to-wheel CI, which is highlighted in Figure 2, can be more economically advantageous due to either reduced carbon tax or LCFS credits. BioFlux pretreatmenv uses less electricity than conventional pretreatment. It also reduces the overall hydrogen consumption in the hydrotreating unit. Using produced naphtha and off gas further reduces CI by eliminating the need for imported natural gas to generate hydrogen.

Figure 3 compares the CI values for various combinations considering soybean oil as the feedstock. Relative to the base case of conventional pretreatment & hydrotreating technologies, using BioFlux technologies can reduce CI by up to 13%. For a 10,000 bpd HVO complex, this translates to a reduction in CO_2 emissions of up to 125,000 tonnes per year.

Figure 2. Main Process Units in the HVO Biorefinery

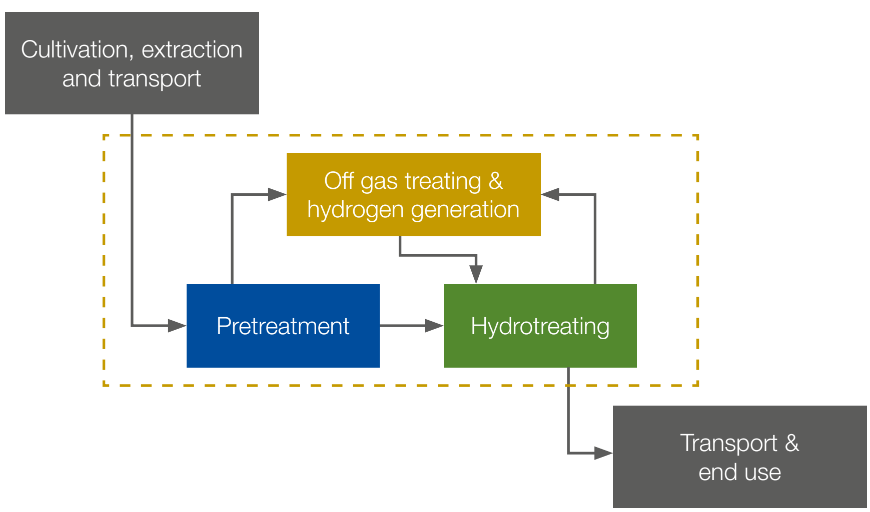


Figure 3. Comparison of Process Carbon Intensity

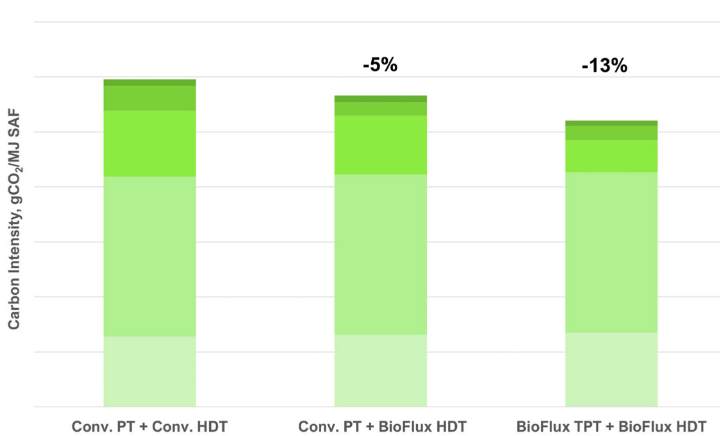
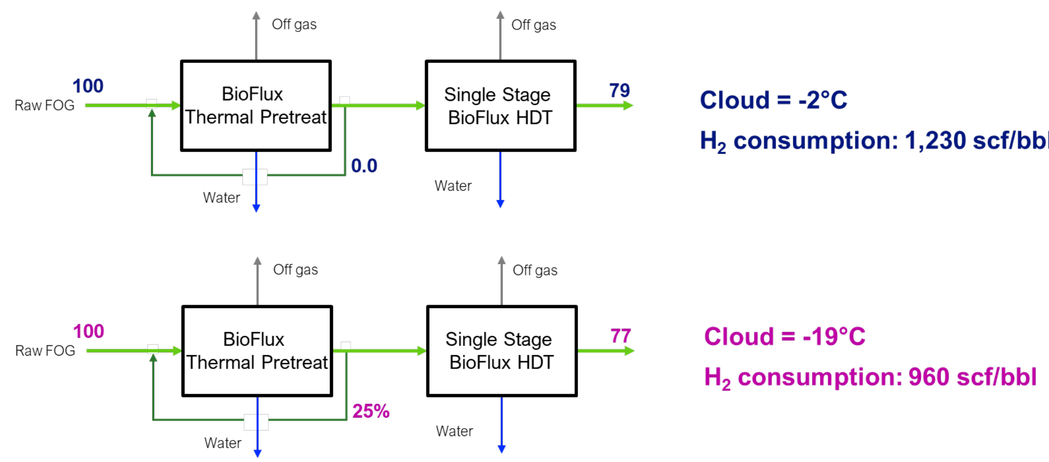


Figure 4. Single-stage hydrotreating with lower hydrogen consumption



Benefits exemplified

With such a significant reduction in hydrogen consumptions, further economic efficiencies can be gained by operators focused on production of HVO. As outlined above, the product from a BioFlux Thermal Pretreat unit is a mix of distillate range hydrocarbons and a portion of unconverted / under-converted feedstock. Thus, distillate hydrocarbons and partially converted product need only minimal treatment to remove the remaining oxygen and tune the material to meet the necessary HVO specifications. What once required two stages of reaction – deoxygenation and isomerization – can now be accomplished in a single reactor. In this scenario, the CAPEX savings can be as much as 50%. Base metal catalyst may also be used for isomerization, which reduces cost as well.

Figure 4 shows how adjusting operating conditions of the PTU, namely the amount of internal recycle, can influence the final product from the HDT. With a once-through design, the BioFlux TPT + HDT can produce a diesel product with -2°C cloud point with ~1,230 scf/bbl (200 Nm3/m3) hydrogen consumption. By recycling the unconverted oils from the reactor, the cloud point and hydrogen consumption are reduced to -19°C and 960 scf/bbl (159 Nm3/m3) respectively.

Your partner in sustainability

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 Thermal Pretreat is a low-CAPEX, low-OPEX solution for removing contaminants from bio-based materials that increases yield and significantly lowers hydrogen consumption. The process offers superior operational stability for extended catalyst life and is suitable for grassroots, revamps, or co-processing units.

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