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White Paper

June 2022

Pretreating renewable
feeds to produce
sustainable clean fuels

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Clean fuel from renewable sources is a critical element in meeting energy requirements of the future. Renewable diesel has become the leading alternative as companies invest in a more environmentally conscious energy supply. Completely fungible with petroleum diesel, renewable diesel from bio-mass based feeds has lower sulfur and higher cetane than its petroleum-based equivalent and can be used without modification to existing infrastructure. Regulations and incentives are encouraging investments, placing renewable diesel and sustainable aviation fuel at the forefront of the clean fuels transition.

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The path to HVO

Hydroprocessing units that generate either Hydrogenated Vegetable Oil (HVO) or SAF use bio-based feedstocks that fall into one of three categories – Fats, Oils, & Greases (FOGs). These materials share similar characteristics despite the source. They are primarily triglycerides, or three fatty acid chains on a glycerol backbone. They can be sourced from plant oils and animal fats as either virgin or recycled materials. Each source is unique in terms of the fatty acid profile, but they are all highly olefinic and contain trace heteroatom contaminants. Some of the typical physical properties of these materials are shown in Table 1. 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. As the trend towards renewable fuels accelerates, the traditional fossil HDT unit is being re-purposed by refiners making the switch to renewable feeds.



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
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

Another alternative is co-processing, whereby a certain percentage of FOGs are combined with fossil diesel for treating in an HDT unit. This mode of operation allows refiners to meet certain commitments related to renewable fuels without investing large amounts of capital. However, FOGs in a co-processing unit are typically limited to ~10-20wt% of the total fresh feed rate. Introducing a higher percentage of bio-based feeds often leads to operational difficulties due to water generation and higher exotherm. Also, cycle times are typically shorter due to premature catalyst deactivation.

Regardless of the manner in which refiners chose to introduce renewable feeds into operation, proper pretreatment of the FOGs is a critical step. The pretreatment unit upstream of a HDT removes the contaminants that can severely influence downstream operations and negatively impact product qualities. Referring to Table 1, properties of particular concern in HDT processes include phosphorus, chlorides, total metals, and moisture content. Multiple processes exist for feedstock purification, but they have been developed primarily with edible fats and oils in mind.

Refining, acid degumming, and bleaching are typical steps used to remove phosphorus and metals. Other processes have been developed, but they use high pressure or introduce water into the system. In either process, though the fatty acid chain primarily remains unconverted and acceptable levels for contaminant removal are difficult to achieve.

Furthermore, when processing in a hydrotreater, olefin saturation, deoxygenation, and isomerization are still required. Renewable feedstocks derived from biological sources are highly olefinic and/or contain high levels of heteroatom contaminants, such as oxygen, nitrogen, sulfur, etc. To produce a valuable product from such highly olefinic and highly contaminated feedstocks, a large amount of hydrogen is required, typically between 1500-2500 scf/bbl. This is up to 300% higher than typical petroleum hydrotreating. Furthermore, these reactions are highly exothermic, generating significantly more heat than typical hydroprocessing processes of petroleum products. All combined, these characteristics of FOGs lead to inefficient HDT operation and limit opportunities for co-processing.

A novel idea

BioFlux® Pretreatment technology, developed by Duke Technologies LLC and licensed by Sulzer, is an alternative process designed to economically treat FOGs and enable more efficient hydrotreating operations. Biomass-based FOGs are thermally cracked 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 mechanical separation (i.e., centrifugation)
- > Lower hydrogen consumption in the downstream hydrotreater
- > No glycerin by-product

The BioFlux® Pretreatment technology is a thermal process that cracks the FOGs. The steps of acid degumming, centrifugation, acidic or supercritical water washing found in other processes are not required in the BioFlux® Pretreatment process. Instead, material is heated and transferred to reactors where the triglyceride molecules are converted into a hydrocarbon-like distillate product. The severity of the reactions may be controlled to fine-tune the product properties. As in the hydrotreating process, aqueous waste and off-gas are generated from the reactions. Unlike other processes, glycerin or other unwanted byproducts are not produced in the BioFlux® Pretreatment unit. 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. Additionally, special phosphorus-trapping catalysts would not be required. An example of the product properties is shown in Table 2.

Typical grassroots HVO units consist of two stages: hydrodeoxygenation (HDO) followed by isomerization. As mentioned above, total hydrogen consumption averages 2'000 scf/bbl in HVO units. However, conversion of the FOGs in the BioFlux® Pretreatment unit can significantly reduce the hydrogen requirements in the HVO unit. By cracking the triglycerides outside of the hydrotreater, both the hydrogen consumption and exotherm are significantly reduced. A low severity operation the BioFlux® Pretreatment unit can reduce hydrogen consumption in the HDT unit by 50%. At maximum severity, the hydrogen consumption can be reduced by 70%. Not only are operating expenses due to hydrogen reduced, this also has potential to significantly reduce

- > Grassroots HVO units will be smaller and more cost-effective, as they require less catalyst and hydrogen per barrel of feedstock.
- > Co-processing in an existing refinery can be accomplished without any modifications to the existing unit.

By generating a distillate-like product requiring only 600 scf/bbl of hydrogen, refiners can produce an HDT feedstock that can be fed directly into existing diesel hydrotreaters (DHT). The only limitation would be upper the capacity limit of the existing unit. Pretreated FOGs produced from other pre-treatment processes might remove contaminants, but they retain the same oxygen and olefin content of the base feedstock, which limits capacity and/or increases investment.

A summary of the pretreatment options is given in Table 3. As shown on the right, the BioFlux® Pretreatment option is the most flexible and cost-effective pretreatment technology. It has the lowest CAPEX of the three options and produces a product that is compatible with existing hydrotreating processes.

Table 2. Pretreatment product properties

	Distillers Corn Oil	Waste Chicken Fat
Phosphorus, ppm	0.7	0.8
Chlorides, ppm	< 0.5	< 0.5
Total Metals, ppm	< 1.0	< 3.0
Cloud Point, °C	-12	-12

Table 3. 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

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, CO₂ 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 1, can be more economically advantageous due to either reduced carbon

tax or LCFS credits. BioFlux® pretreatment 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 2 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 11%. For a 10'000 bpd HVO complex, this translates to a reduction in CO₂ emissions of up to 130'000 tonnes per year.

Figure 1. Main Process Units in the HVO Biorefinery

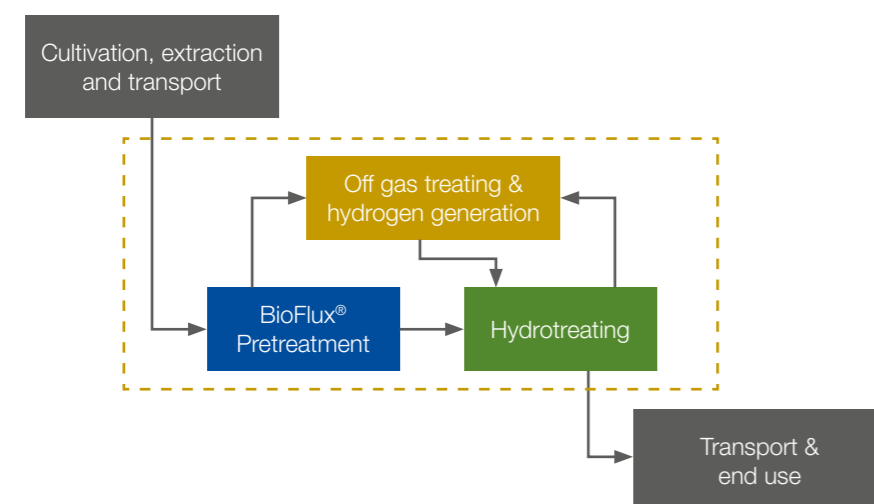
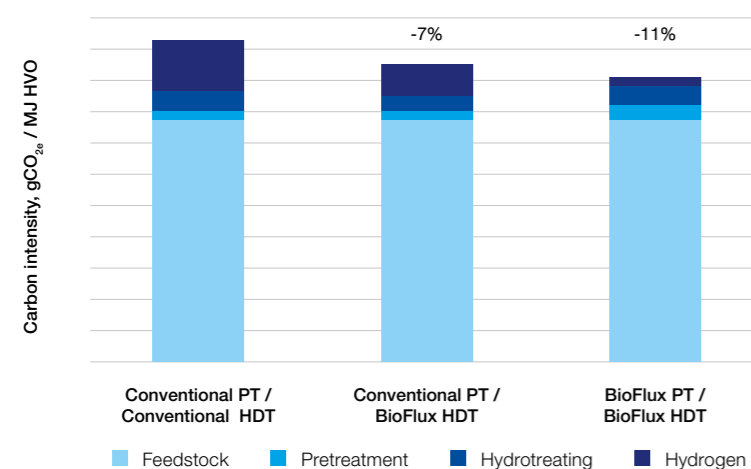


Figure 2. Comparison of Process Carbon Intensity



Benefits exemplified

To further highlight the benefits of co-processing with BioFlux® Pretreatment technology, consider the case where a refiner wished to import a certain amount of bio-mass based feedstocks into their existing hydrotreater. With economics already unfavorable due to the high feedstock costs, the option for edible oil pretreatment was simply too expensive and the equipment too complicated. Furthermore, the unconverted nature of the FOGs either 1) limited capacity in the existing unit or 2) required the construction of a second stage isomerization reactor. Similarly, for the fat splitting technology, the product from the hydrolysis-based pretreatment unit was still in the form of a fatty acid molecule. This product would require olefin saturation, oxygen removal and isomerization in the existing unit. Without considerable investment in the HDT, the revamped unit capacity would be greatly limited post-startup.

However, with BioFlux® Pretreatment technology, the refiner in this example will be able to generate a distillate range material that can be fed directly to the existing DHT. At the same time, the existing reactor will be filled with new catalyst. Once completed, the unit will be able to maintain existing capacity at similar or extended cycle lengths without addition of another catalyst bed or dedicated isomerization reactor. BioFlux® Pretreatment technology has given this refiner the lowest cost and most flexible option for introducing FOGs into the existing DHT.

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® Pretreatment technology 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. To learn more about the BioFlux® Pretreatment 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:

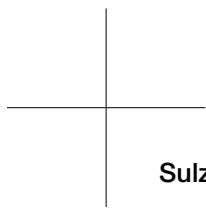
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