LUBRICITY CHALLENGES OF RENEWABLE DIESEL FUELS

The development of renewable sources of fuel has been pivotal in the reduction of greenhouse gas emissions, as the demand for cleaner fuels continues to grow. With the founding and creation of renewable diesel, processes performed using diesel now have a suitable substitute that not only exceeds the performance of traditional petrol diesel but is also cost-efficient. One highly effective and reproducible method of producing renewable diesel involves hydrotreating biomass-derived materials such as vegetable oils [1]. The process of hydrotreating involves the removal of oxygen and other heteroatoms, such as sulfur, by selectively reacting these less desirable materials with hydrogen in a reactor at relatively high temperatures and pressures. [2] A schematic of the hydrotreatment process is shown in Figure 1.

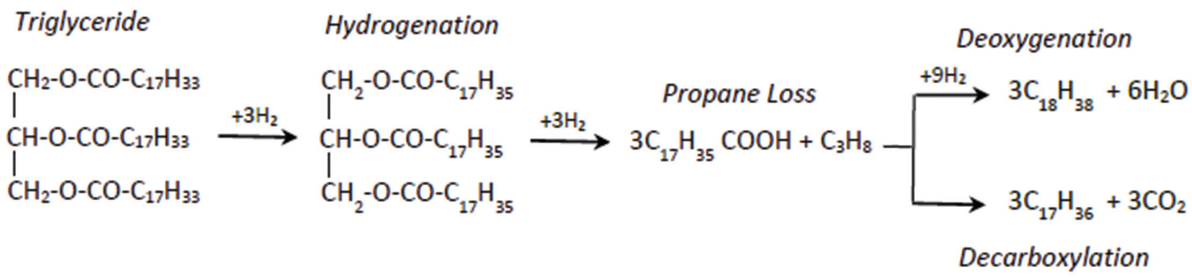
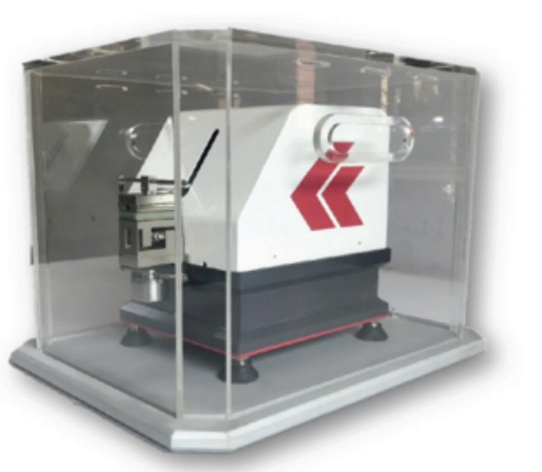


Figure 1. Hydrotreating Process in the Production of a Renewable Diesel [6]

One drawback of this process is the poor lubricity of newly composed renewable diesel. Considering that sulfur acts as a lubricant in fuel, the low sulfur content in renewable diesel will lead to low lubricity. Additionally, the oxygen-containing components removed during hydrotreating have been studied and proven to significantly reduce wear and improve lubricity to acceptable levels [3]. An effective and reproducible way of measuring the lubricity of diesel fuel is described in the test method ASTM D6079 [4]. By using a High Frequency Reciprocating Rig (HFRR) we can ensure a diesel fuel's lubricity is within the requirements as per the Standard Specification for Diesel Fuel Oils in ASTM D975 (<520 μm) [5]. The HFRR instrument and the ASTM D6079 test method involves rubbing a metal ball in an oscillating motion against a platform metal disk under known conditions while fully immersed in the sample heated to 60°C. The output value from HFRR testing is the wear scar diameter, measured in microns. The wear scar diameter is observed and measured after a test by looking at the ball under a microscope or digital camera and averaging the width and the length of the small blemish formed during testing. An unadditized renewable diesel sample typically has an HFRR wear scar diameter over 700 μm, which is far above the permissible level in any of the diesel fuel specifications, typically 450 to 520 μm. Therefore, lubricity improver additives are commonly used with renewable diesel [1].



The HFRR instrument (Figure 2) and the ASTM D6079 test method involves rubbing a metal ball in an oscillating motion against a platform metal disk under known conditions while fully immersed in the sample heated to 60 degrees C.

The lubricity of a fluid is often defined as the fluid's ability to reduce friction between that fluid and the solid surface during motion. Lubricity is a key fuel property due to the potential to increase the longevity of a part as well as ensuring maximum performance of the system. When a fuel's lubricity value does not conform to regulations, metal parts are likely exposed to each other, resulting in wear or scarring. In the late 2000s, the lubricity of fuels became a controversial topic due to the increased gas emissions. The high sulfur content in petroleum fuels has been identified as a cause for harmful exhaust emissions, which has led to strict regulations on the allotted sulfur content in diesel fuels globally. A strict regulation was placed to keep sulfur content at a low 15 ppm, according to EPA regulations [7]. While sulfur is a pertinent lubricating agent in petroleum products, regulations have prompted the removal of most of the sulfur in refinery processes, resulting in a loss of fuel lubricity. Due to these lubricity challenges, there is a need for continued research on how renewable diesel can be improved to replace the traditional petroleum diesel.

The growth in production and usage of renewable diesel shouldn't be a surprise as renewable diesel's composition is shockingly similar to traditional crude oil-derived diesel. When atoms such as sulfur, nitrogen, and oxygen are removed during the hydrotreating process, the triglyceride molecules from the base oil are converted into paraffinic hydrocarbons (alkanes) [8]. Traditional petrodiesel contains a combination of hydrocarbons (predominately paraffins) with fewer cycloalkanes and aromatic hydrocarbons. The n-paraffin molecular chain is the base of both fuel types. As shown in Figure 3, renewable diesel maintains and, in some cases, exceeds the performance of traditional diesel fuel.

However, the lubricity of renewable diesel is one property that is negatively affected during its production, which is often less than the ASTM diesel fuel specification of 520 μm max wsd. One paper from 2014 illustrates the differences in lubricity between renewable diesel in the form of hydrotreated vegetable oil (HVO)

Property	No. 2 petroleum diesel	Renewable diesel
Carbon, wt.%	86.8	84.9
Hydrogen, wt.%	13.2	15.1
Oxygen, wt.%	0.0	0.0
Specific Gravity	0.85	0.78
Cetane no.	40–45	70–90
T_{90}, °C	300–330	290–300
Viscosity, mm^2/s. @ 40 °C	2–3	3–4
Energy content (LHV)		
Mass basis, MJ/kg	43	44
Mass basis, BTU/lb.	18,500	18,900
Vol. basis, 1000 BTU/gal	130	122

Figure 3. Properties of Traditional Diesel and Renewable Diesel [9]

Property	Unit	Fossil diesel	HVO
Density 15°C	kg/m^3	818,2	778,9
Cloud Point	°C	-29	-19
Cold Filter Plugging Point	°C	-29	-19
Viscosity 40°C	mm^2/s	1,843	2,901
Sulfur Content	mg/kg	8,5	<1
Flash Point	°C	60	83
Cetane Number	-	49,1*	79,6
Monoaromatic Content	wt-%	16,5	<0,2
Diaromatic Content	wt-%	1,5	<0,1
Tri+ Aromatic Content	wt-%	<0,1	<0,10
Polyaromatic Content	wt-%	1,5	<0,1
Total Aromatic Content	wt-%	18	<0,2
HFRR	µm	653**	580**
Initial Boiling Point	°C	167	193
5% (V/V) recovered	°C	189	237
10% (V/V) recovered	°C	195	253
20% (V/V) recovered	°C	204	267
30% (V/V) recovered	°C	212	274
40% (V/V) recovered	°C	222	279
50% (V/V) recovered	°C	230	282
60% (V/V) recovered	°C	240	284
70% (V/V) recovered	°C	252	287
80% (V/V) recovered	°C	267	290
90% (V/V) recovered	°C	288	292
95% (V/V) recovered	°C	305	294
Final Boiling Point	°C	320	299
% (V/V) recovered at 180°C	% (V/V)	1,5	<0,1
% (V/V) recovered at 250°C	% (V/V)	68,3	9

* Requires cetane improver to meet EN590 cetane requirement ≥ 51,0

** HFRR without any lubricity additives

Figure 4. Fuel Properties Comparison [10]

and regular fossil diesel [10]. As shown in Figure 4, the lubricity of regular petroleum diesel and HVO using HFRR are 653 µm and 580 µm, respectively [10]. It is important to note that these values are taken without the addition of any lubricity additives. Renewable diesel on its own fails to meet ASTM diesel fuel regulations for lubricity wear-scar and therefore requires additives to improve this crucial measurement.

Blending hydrotreated vegetable oil (HVO) derived renewable diesel with petroleum diesel improves the lubricity, but to maximize environmental benefits, we need to investigate effective additives to improve the lubricity of pure renewable diesel, which does not meet ASTM specifications. Testing the effectiveness of these additives is done by comparing their wear scar values to those of untreated HVO renewable diesel. The sliding wear is determined in the test method ASTM D6079 [4]. The larger the wear scar value is, the worse the lubricating properties of the fuel are [11]. Two additives, rapeseed methyl ester (RME) and Jatropha curcas L. oil (JCL), are tested to determine their effects on lubricity. Both biodegradable oil-derived substances were subjected to an HFRR test to determine the amount of friction present and wear scar on the surface. As shown in Figure 5, JCL presents outstanding

	X-axis	Y-axis	Average
Low lubricity diesel fuel (LLDF) + No additive	635	673	654
LLDF + 0.5% JO	365	284	325
LLDF + 0.7% JO	253	190	222
LLDF +1 % JO	238	158	198

Figure 5. Additive JCL effect on wear scar [12]

results in improving lubricity when blended with a low lubricity diesel fuel, such as renewable diesel. A low lubricity diesel fuel combined with 1% JCL yields a wear scar of 198 µm which is an approximate 550 µm reduction in the lubricity measurement. Increasing the concentration of the JCL oil in the base fuel from 0.5 % to 1.0% resulted in enhanced lubricity as shown by the reduced wear scar [12]. The addition of RME to a base fuel, as depicted in Figure 6, also shows a reduction in wear scar and therefore improved lubricity. The concentration of RME needed for such change to occur is quite high. According to D975, 1% or less added component can be considered an additive. Addition of greater than 1%, particularly 5-15%, is not an additive, but rather a fuel component [5]. In this study RME can be considered as a fuel component based on the amounts present. The inclusion of 15%, by weight, RME in the base fuel showed the most improved results of an approximate 160 µm wear scar diameter, although any improvement below 300 µm is similarly performant. All values tested with additives included were within the requirements of the Standard Specification for Diesel Fuel Oils in ASTM D975.

In testing for the coefficient of friction, JCL performs well with an impressive average of 0.11. RME shows a sufficient average of about 0.14 [14]. A lower coefficient of friction value often indicates better lubrication. Both additives show excellent lubricity improving properties. The addition of Jatropha curcas L. oil and rapeseed methyl ester could aid in solving the challenging lubrication problem in renewable diesel fuels.

Some other critical facts to mention about lubricity improvers are that lubricity typically improves with a longer chain length additive and the lubricity also improves with the increased presence of double bonds in the additive [15]. Additionally, it has been studied that different oxygenated compounds have a greater effect on the lubricity of diesel fuels. They are ordered in regards to their lubricity improving potential (COOH > CHO > OH > $COOCH_3$ > C=O > C-O-C) [15]. One similarity between all the functional groups is the inclusion of oxygen in its structure. The addition of oxygen-containing compounds remaining after the refining process can greatly affect a fuel's lubricity.

Another solution to this challenging lubrication problem is the combination of renewable diesel with other diesel blends. As mentioned previously, renewable diesel blended with traditional petroleum diesel does improve lubricity, but this combination is not the most environmentally friendly. Most recently, the combination of renewable and biodiesel has been explored. Biodiesel production involves the transformation of long chain triglyceride fatty acids into long chain fatty acid methyl esters, or FAME, by the process of transesterification. Biodiesel has exhibited excellent lubricity in practice. Oxygen and other heteroatoms are not removed during this process, which is the principal reason for the increased lubricity. As previously mentioned, renewable diesel requires additives to reach lubricity regulations. REG ultraclean diesel is a new blend of renewable diesel and biodiesel that has improved properties such as a higher cetane number, a longer engine life, reliable operation in colder temperatures, and most importantly lubricity [16]. This name is certainly misleading as biodiesel is not fully environmentally friendly. Some biodiesels have been shown to give off a significant amount of nitrogen oxide

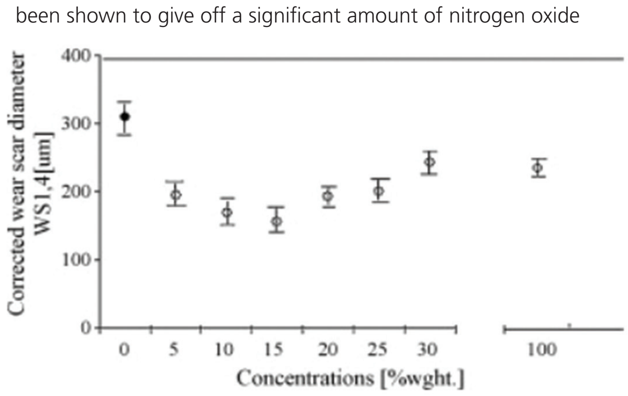


Figure 6. Additive RME effect on wear scar [13]

(NO_x) in the exhaust during combustion [17]. This alone provides a reason to expand the research on renewable diesel as it is much better at preventing harmful emissions. REG ultra clean is a clear improvement over traditional crude oil-derived diesel, but there are still plenty of things that can be improved.

Renewable diesel has the ability to match and exceed the performance of traditional petroleum diesel in specific categories. Correcting the lubricity of both renewable diesel and traditional petroleum is a challenge. Fortunately, there is a multitude of different lubricity additive options that can vastly improve the lubricity characteristics of these diesels. When blended with highly effective biodegradable fuel components, such as RME, the poor lubricity of untreated renewable diesel can be corrected to meet ASTM regulations. In addition, by offering a significant reduction of greenhouse gas emissions and other major environmental benefits, renewable diesel has the potential to become the next dominant source of energy for transportation in the future.

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About the Authors

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 25 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, NLGI, INSTMC, The Energy Institute and The Royal Society of Chemistry.
A Ph.D in Chemical Engineering from The Penn State University (https://www.che.psu.edu/news-archive/2018/alumni-spotlight-raj-shah.aspx) and a Fellow from The Chartered Management Institute, London, Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK. An adjunct professor at the Dept. of Material Science and Chemical Engineering at State University of New York, Stony Brook, Raj has over 400 publications and has been active in the petroleum field for 3 decades.

More information on Raj can be found at https://www.petro-online.com/news/fuel-for-thought/13/ koehlerinstrument-company/dr-raj-shah-director-at-koehler-instrumentcompany-conferred-with-multifariousaccolades/53404


Nabill Huq


Anthony Schevon

Mr. Nabill Huq and **Mr. Anthony Schevon** are students of Chemical engineering at SUNY, Stony Brook University, where Dr. Shah is the chairman on the external advisory board of directors, and they are currently part of the thriving internship program at Koehler Instrument Company, in Long Island, NY.


David Forester

Mr. David Forester recently retired after 44 years' experience in the fuel and refining additive business. He has over 35 US patents on development of diesel and jet fuel additives, refinery antifoulants, and other refinery and process related additives. He has designed, implemented and/or automated many fuel test methods, including many ASTM standards. Mr. Forester most recently received the ASTM Award of Merit.

He has been a member of ASTM Committee D02 for over 25 years and currently serves as Chairman of Subcommittee D02.14 Stability and Cleanliness of Liquid Fuels. He served along with Dr. Shah as the editor of the ASTM bestseller "The Fuels and Lubricant Handbook" published in 2019. More information on this can be found at https://www.petro-online.com/article/analytical-instrumentation/11/petro-industry-news/astmrsquos-long-awaited-fuels-and-lubricants-handbook-2nd-edition-now-available/2792

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company • Holtsvile, NY 11742 USA • Email: rshah@koehlerinstrument.com • **Web: www.koehlerinstrument.com**