

Electrochemical Production of Hydrocarbons for Lubricants and Fuels from Biological Feedstocks

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ABSTRACT

Altranex Corporation produces hydrocarbons from biologically-derived fats, oils and greases. Through a patented combination of electro- and thermo-chemical processes, Altranex can produce hydrocarbons for use as high-performance lubricant base oils, mineral oils, drop-in renewable fuels, and other products. The core innovation in the Altranex process is an electrolysis process that simultaneously removes oxygen from free fatty acids and dimerizes the radicals to form longer hydrocarbon chains in an economical process. The processes are feedstock agnostic and can tolerate fats, oils and greases with very high free fatty acid content. The types and size of hydrocarbons produced depends on the feedstock selection. Altranex has successfully produced hydrocarbons from soybean, canola, tallow, lard, coconut, palm, and even used cooking oil.

A primary focus of the Altranex-Valvoline partnership is the production of base oils for automotive and industrial lubricants. Base oil constitute 80-90% of lubricating oil with the balance being additives that impart characteristics for specific applications such as crankcase oil, transmission fluid and metal cutting oils. The Altranex process enables production of base oils with a very narrow size distribution leading to superior viscosity characteristics and excellent low temperature properties. Using Altranex's base oil, Valvoline has formulated a multi-grade motor oil that has

- 1) characteristics comparable to synthetic motor oils;
- 2) favourable production cost structure; and
- 3) lower greenhouse gas (GHG) emission profile that petroleum-based motor oils.

Other products from Altranex's process technology include synthetic mineral oil and renewable diesel fuel. Synthetic mineral oils produced from renewable feedstock are high-purity low viscosity oils and the renewable diesel is a drop-in replacement that is oxygen-free and has a pour point less than -20 C.

Keywords: *renewable lubricants, life cycle analysis, electrochemistry, renewable diesel, hydrocarbons sustainability, electrochemistry*

1 ALTRANEX PROCESS

The Altranex process is a combination of several chemical processes applied to plant oils or animal fats to produce hydrocarbons that can be used as lubricant base oils, renewable fuels, chemical precursors and other products. Depending on the final products, the process includes different chemical steps and their sequence. The process for lubricant base oil production consists of four major steps: (i) hydrolysis of plant-based oils or animal fats to produce free fatty acids (FFAs), also known as fat splitting; (ii) electrolysis of the fatty acids to build long-chain hydrocarbons, (iii) hydrofinishing, resulting in skeletal isomerization of long-chain hydrocarbons to yield large, saturated, branched hydrocarbons ideal as lubricant base oil, and (iv) separation of products from a hydrocarbon mixture. The process is schematically depicted in Figure 1. The parameters of the electrolysis and hydrofinishing steps can be adjusted to maximize the yield of the targeted product.

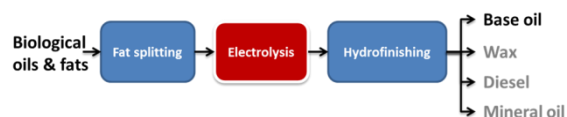
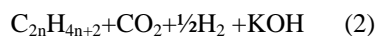
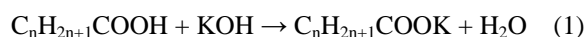


Figure 1: Process pathway for the conversion of plant-based oil to lubricant base oil.

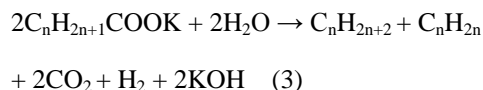
The fat splitting step involves the reaction of water with triacylglycerol (plant oil or animal fat, also known as triglyceride) to yield FFAs and glycerol. Altranex used the base-catalyzed reaction approach (also called saponification), which involves treating the oil with sodium or potassium hydroxide, which splits the fat and yields salts of the fatty acids. However, other fat-splitting processes will work as well. Neutralizing these with mineral acid yields FFAs, which separate as an oily layer above the

reaction mixture. On the industrial pilot-scale stage, the focus is shifted to a continuous steam hydrolysis process. This process is the cleanest since it does not require a catalyst, which would otherwise need to be separated from the FFAs stream before it is passed on to the next process. Furthermore, the steam hydrolysis directly produces FFAs, not their salts, eliminating the need for using mineral acids.

The second step in the Altranex process for lubricant base-oil production is an electrochemical decarboxylation of the FFAs, converting them to hydrocarbons, also known as Kolbe electrolysis. The process includes the conversion of FFAs, supplied from the fat splitting stage, into their salts by reacting with potassium or sodium hydroxide (1), and the electrolysis of these salts using a platinum catalyzed anode to produce long-chain hydrocarbons (2).

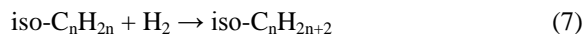


Reactions (1) and (2) show the process for fully saturated (no double bonds) FFAs. The same process applies for a variety of fatty acids, saturated and unsaturated (n=9–23). The side reaction for the process (2) is an electrochemical process with production of short-chain hydrocarbons (alkane and alkene):



The hydroxide released in reactions (2) and (3) converts the new portion of FFAs to salt, which allows continuous running of the process with constant FFAs supplying, and the hydrocarbons and gases separating. Long- and short-chain hydrocarbons form the liquid phase, immiscible with a reaction mixture. These hydrocarbons are separated gravimetrically from the reaction mixture.

The third step in the Altranex process is the hydrofinishing of the mixture of long- and short chain hydrocarbons produced in the electrolysis step. Hydrofinishing includes a skeletal isomerization of hydrocarbons (4) – (6) to achieve good cold-weather properties (low cloud point) of lubricants and fuels, and hydrogenation (saturation) of double bonds (7) to ensure high chemical stability and resistance to oxidation during storage.



Reactions (4) – (7) apply for both long- and short-chain hydrocarbons (n=9–46). Isomerizing the hydrocarbons is done by dehydrogenating the chain in the presence of a platinum catalyst to produce intermediate olefins (4), which in the presence of a solid acid catalyst will protonate to give a carbenium ion (5), which then undergoes skeletal rearrangement, followed by regeneration of olefin in an elimination reaction (6). Finally, the olefin is hydrogenated in the presence of molecular hydrogen to yield the isomerized saturated hydrocarbon (7).

Reactions (4) – (7) take place in a single flow-through reactor with bifunctional catalyst containing two components: a platinum metal catalyst to support dehydrogenation-hydrogenation reactions (4) and (7), and an alumina-silica solid acid catalyst that also imparts the molecular size selectivity toward linear hydrocarbons, making the reactions (5) and (6) more efficient.

Separation of hydrocarbon products is performed in two steps: separation of short-chain hydrocarbons (renewable fuels) by evaporating at low pressure, and dewaxing the remaining liquid phase by filtration at low temperatures to produce lubricant base oils.

2 LUBRICANT FORMULATION AND PROPERTIES

The goal of this project is to synthesize high-quality group III base oil that is produced from renewable sources, such as plants. Currently, renewable group III oil is very difficult to find due to the stringent description of the material (Table 1).

Group	Sulfur, Wt %		Saturates	VI
I	>0.03	and/or	<90	80 – 119
II	≤ 0.03	and	≥90	80 – 119
III	≤ 0.03	and	≥90	≥120
IV	All Polyalphaolefins (PAOs)			
V	All Stocks Not Included in Groups I-IV (Pale Oils and Non-PAO Synthetics)			

Table 1: API base stock categories.

In addition, group III base oils can be used to formulate motor oils that are allowed to be called “synthetic” which is a term that ensures a motor oil will be of the highest quality. So these group III base

oils must fit within a set of physical parameters and possess properties that can make a great motor oil.

First, a group III base oil must contain very little sulphur and a high degree of saturates, meaning that it must have a very small percentage of double bonds or aromatic moieties in the molecules: it must be largely aliphatic. Also, it must be all-hydrocarbon. Most renewable oils found in nature contain oxygen and are classified as esters. Removing the oxygen atoms requires a form of synthetic chemistry so it increases the complexity of creating molecules with base oil properties. The chemical reaction that removes oxygen must also give a final product that is oxidatively stable at high temperatures and very fluid at low temperatures, as that is what is required of a synthetic motor oil. Additionally, the base oil must have a viscosity index (VI) of more than 120. Viscosity index is an indication of how a fluid's viscosity changes with changing temperature. The less it changes, the higher the VI of the fluid. In general, higher VI makes for better base oil. Beyond these basic minimum specifications, we are trying to create high quality group III base oil. That means we must exceed the performance characteristics of typical group III base oils. One additional way to accomplish this is with a material that has less volatility in a Noack test (ASTM D5800). In summary, we want a hydrocarbon material that, when compared to current group III base oils, has greater oxidative stability, is more fluid at low temperatures, is less volatile, has a better viscosity index and is produced from renewable sources.

The development and testing of this renewable base oil is an iterative process. We have analyzed one sample already. The results of some testing on the pure base oil compared to commercial group III base oils are in Table 2.

These first results demonstrate that we are at least in the ballpark. The Altra-BASE material compares well to the other group III base oils except for one parameter: viscosity index. The Altra-BASE viscosity index is significantly higher than the commercial oils. In addition, the synthetic method allows for us to improve the Noack just by altering the feedstock used, so improving that parameter should be quite straightforward. This material has the potential to become a very high quality renewable group III base oil that can be formulated into a top of the line synthetic motor oil.

Property	Test Method	4 cSt	6 cSt	Altra-BASE
Appearance	Visual	B & C	B & C	B & C
Gravity, API @ 60C	D-1298	38.2	36.5	39.2
Density @ 15C, kg/l	D-4052	0.834	0.8423	0.827
Flash Point, COC, C	D-92	217	228	180
Viscosity @ 40C, cSt	D-445	19.57	35.52	11.27
Viscosity @ 100C, cSt	D-445	4.23	6.4	3.62
Viscosity Index	D-2270	122	133	240
CCS Viscosity @ -30C, cP	D-2602	1500	4700	2073
Pour Point, C	D-97	-18	-12	-15
Colour	D-1500	L-0.5	L-0.5	colourless
Sulphur, wt.%	D-4294	0.001	0.001	<0.0001
Noack, wt.% loss	D-5800	14.5	6	12
Water Content, wt.%	D-95	0.01	0.01	0.1
SMD % Off @	D-2887			
	0	331	317	305
	10%	379	423	458
	20%	393	440	485
	50%	419	471	488
	90%	462	525	490

Table 2: Comparison of Altra-BASE to Group III base oil characteristics. Note the extraordinarily high viscosity index that Altra-BASE exhibits.

The next step in assessing the quality and performance of this renewable base oil is to formulate some motor oils using Altra-BASE. These motor oils would be based on current commercial Valvoline Synpower formulations, but they would contain a certain percentage of Altra-BASE replacing current synthetic base oil. The specific tests we would use to test the Altra-BASE formulations to our current commercial synthetic motor oil would be:

- Oxidative stability (PDSC)
- Low temperature pumping (MRV)
- Low temperature cranking (CCS)
- Pour point (response to current PPDs)
- Volatility of finished oil (Noack)
- Biodegradability (OECD 301B)
- Cooling profile (Rheometer, scanning brookfield)
- Contribution to fuel economy (friction and wear, sequence VIE)

3 LIFE CYCLE ANALYSIS

Life cycle assessment (LCA) is a valuable tool that is able to evaluate the overall GHG emissions throughout the entire life cycle of a process or a product, from cradle to grave [1]. It has been applied to the Altranex process to quantify the GHG emissions during the production of the lubricating oil and renewable diesel, and to compare the GHGs to those from their petroleum-based counterparts. The LCA result will also help the industry to better understand opportunities to reduce life-cycle GHG emissions by changing parameters around feedstock procurement or process conditions.

System Boundary and Functional Unit

The system boundary for the production of the Altranex products is shown in Figure . It is cradle to gate, covering all potential GHG emission sources such as oilseed cultivation, feedstock oil extraction, transportation, etc. The functional unit is the production of 1 kg of the lubricating oil or renewable diesel. The allocation method is mass-based allocation.

Life cycle inventory (LCI)

The life cycle inventory data used in this LCA study are sourced from the original process data, GHGenius and its database (version 4.0.3) [7],

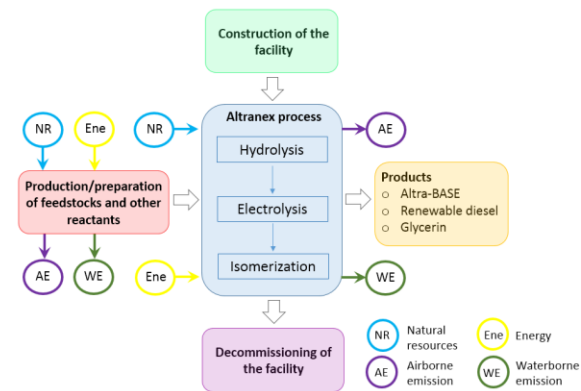


Figure 2: Life cycle analysis system boundary for the Altranex process.

SimaPro (version 8.0.1. developed by the PRÉ Consultants in Netherlands) [11] combined with ecoinvent [2] and USLCI databases [10], and literatures. The input and output inventory for the production of 1 kg of lubricating oil or renewable diesel from 70 wt% soybean oil and 30% tallow is summarized in Table . The total GHGs listed in the last column of the table is calculated by multiplying the amount of each input/output with its perspective GHG emission factor.

The GHG emission factor of the feedstock oil (i.e. soybean oil or tallow) is the sum of the upstream GHG emission and an additional GHG credit (Table). The upstream GHGs as obtained from GHGenius [7] have covered all GHGs emitted during the process of growing oilseed and extracting oils; the GHG credits of co-products, such as the protein meal produced during the oil extraction step, are also included. Since the growth of plant absorbs CO₂ from the atmosphere, an additional CO₂ credit is included in the inventory, as has been done by [8]. The carbon content of the soybean oil is 77%. Assuming all carbon is from the atmosphere, for every kg of oil produced, 2.82 kg CO₂ is sequestered in the plant,

similar to that reported by Miller and co-workers (2.44 kg CO₂/kg soybean oil). As for tallow, the carbon is from biogenic sources as well, so that a similar GHG credit (-2.82 kg CO₂-e/kg oil) is applied. Therefore, the overall calculated GHGs for soybean oil and tallow are -1.99 kg CO₂-e/kg oil and -3.6 kg CO₂-e/kg oil, respectively. It should however be noted that this GHG benefit typically accrues to the consumer from using the products but not accrues to the producers. It is included in this study to evaluate the maximum GHG reduction with the production of the innovative lubricating oil and renewable diesel.

Name	Amount	GHG factor	Total GHG
Output			
Altranex product	1 kg		
Glycerine ¹	1.50E-01 kg	2.67 kg CO ₂ -e/kg	-0.40 kg CO ₂ -e
Input			
Construction of the plant	1.01E-09 p ²	5.00E06 kg CO ₂ -e/p ³	0.005 kg CO ₂ -e
Raw materials and resources			
Soybean oil	1.00 kg	-1.99 kg CO ₂ -e/kg	-2.00 kg CO ₂ -e
Tallow	0.43 kg	-3.6 kg CO ₂ -e/kg	-1.55 kg CO ₂ -e
Ethanol	7.87E-03 kg	1.24 kg CO ₂ -e/kg	0.01 kg CO ₂ -e
Hydrogen	1.26E-02 kg	2.22 kg CO ₂ -e/kg	0.03 kg CO ₂ -e
Utilities			
HP steam (6000 kPa) ⁴	0.51 kg	0.145 kg CO ₂ -e/kg	0.07 kg CO ₂ -e
MP steam (1000 kPa) ⁴	2.62 kg	0.145 kg CO ₂ -e/kg	0.38 kg CO ₂ -e
Electricity	2.36 kWh	0.703 kg CO ₂ -e/kWh ⁵	1.66 kg CO ₂ -e
Transportation ⁶	0.14 tkm	0.093 kg CO ₂ -e/tkm	0.013 kg CO ₂ -e
Emissions			
Wastewater	8.61E-04 m ³	0.722 kg CO ₂ -e/m ³	0
Acetic acid	1.05E-02 kg		
Carbon dioxide	2.16E-01 kg	1 kg CO ₂ -e/kg	0.22 kg CO ₂ -e
Hydrogen	5.46E-03 kg		
Total			-1.57 kg CO₂-e

Notes:

¹ Glycerine as a co-product is credited with GHG emissions that are associated with its production through traditional pathways.

² Assuming the lifetime of the facility is 30 years, and it operates 330 days per year.

³ Estimated from GHGs for the construction of an oil mill and a vegetable oil esterification facility in the ecoinvent database, ranging between 3.27E06 kg CO₂-e/p and 5.21E06 kg CO₂-e/p. Both facilities have a production capacity of 63 tonnes per day.

⁴ Calculated from the enthalpies of saturated steam (6000 kPa or 1000 kPa) and saturated water at room temperature. Assuming 1.17 kg of tap water is needed to make 1 kg of steam, and all heat is provided by natural gas with a heat transfer efficiency of 80%, so that 3.97 MJ of heat is needed to produce 1 kg of steam.

⁵ Based on the electricity mix composition in Alberta, Canada.

⁶ Assuming feedstocks (soybean oil and tallow) are shipped by diesel-powered truck with a shipping distance of 100 km.

Table 3: Life cycle inventory for lubricating oil and renewable diesel production.

Parameter	Unit	Soybean oil	Tallow
Upstream GHG results (from GHGenius)	kg CO ₂ -e/GJ	20.47	-19.94
Heating value (HHV)	MJ/L	36.93	34.39
Density of oil	kg/L	0.915	0.884
Calculated upstream GHG	kg CO ₂ -e/kg oil	0.83	-0.78
Additional GHG credit	kg CO ₂ -e/kg oil	-2.82	-2.82
Overall GHG emission factor	kg CO ₂ -e/kg oil	-1.99	-3.6

Table 4: GHG emission factors of feedstock oils.

Results – GHG reduction compared to the baseline

As shown in Table , the GHG emission per kg of lubricating oil or renewable diesel production is *-1.57 kg CO₂-e* when using 70% soybean oil and 30% tallow as the oil source. In order to quantify the GHG reduction, two baseline GHG emissions from the production of their petroleum-based counterparts were selected for the lubricating oil and renewable diesel, which are 1.67 kg CO₂-e/kg (diesel) [7] and 1.18 kg CO₂-e/kg (lubricating oil) [2], respectively. Correspondingly, the GHG savings are calculated to be *2.75 kg CO₂-e/kg* for the lubricating oil and *3.24 kg CO₂-e/kg* for the renewable diesel.

Results – effects of different oil sources and electricity mix compositions

Of all the input/output GHG emission sources investigated, feedstock oils and electricity are the two items that generate the most significant impacts on the overall GHGs of the Altranex products (Table). The current LCA model calculates GHG savings based a single type of oil mix (i.e. 70% soybean oil and 30% tallow) and employs the electricity mix composition in Alberta as the default case, while it is not likely to be representative of other oil sources and electricity compositions in other regions. As such, more feedstock oils and different power generating sources are investigated, and the results are shown in Table . The overall GHGs from different oil sources follow an order of tallow < canola oil < camelina oil < soybean oil < jatropha oil, consistent with the trend of upstream GHG emission factors of the oils, which is because that the lower the upstream GHG of an oil source, the more GHG credit there will be when oil is utilized in the Altranex process. As for the GHG emission from different electricity mix compositions, the following order is observed: hydro < nuclear < wind < wood chips < biogas < natural gas < hard coal. Compared to a region where power is generated from coal, 2.38 kg CO₂-e GHG reduction can be achieved for every Altranex product produced in a region relying on hydropower.

	GHG emission factor	GHG per kg of Altranex products
Oil source	kg CO ₂ -e/kg	kg CO ₂ -e/kg
100% soybean oil	-1.99	-0.91
100% canola oil	-2.54	-1.71
100% jatropha oil	-1.12	0.34
100% camellia oil	-2.44	-1.59
100% tallow	-3.6	-3.13
Electricity mix composition	kg CO ₂ -e/kWh	kg CO ₂ -e/kg
100% hard coal	1.027	-0.81
100% natural gas	0.516	-2.01
100% nuclear	0.021	-3.18
100% hydro	0.013	-3.19
100% wind	0.037	-3.14
100% biogas	0.298	-2.53
100% wood chips	0.263	-2.61

Table 5: Effects of oil sources and electricity mix compositions on the overall GHG of Altranex products [2, 7]

	Light vehicles in Canada (gas)	Vehicles in US		
		Passenger vehicles (gas)	Light trucks (gas)	Heavy-duty trucks (diesel)
Fuel consumption rate (litres/100 km)	10.6 ^[9]	9.76 ^[41]	13.6 ^[41]	39.64 ^[7]
Annual driving distance (km)	15153 ^[9]	19312 ^[41]	24140 ^[41]	402335 ^[5]
Fuel consumption rate with Altranex lubricating oil (litres/100 km)	10.39	9.57	13.33	38.86
Annual fuel savings per vehicle (litres)	31.5	37.0	64.4	3127.2
CO ₂ emission factor (kg CO ₂ -e/litre of fuel)	2.29 ^[3]	2.35 ^[41]	2.35 ^[41]	2.68 ^[6]
Annual CO ₂ savings per vehicle (kg CO ₂ -e)	72.14	86.95	151.34	8380.90
Annual Altranex lubricating oil consumed per vehicle (kg) ⁷	4.30	5.49	6.86	70
Unit GHG saving per kg of Altranex lubricating oil utilized (kg CO ₂ -e/kg)	16.75	15.80	22.02	119.73

Note: ⁷ Based on average oil quantity and change frequency.

Table 6: GHG savings through the use of Altranex lubricating oil in Canadian and US vehicles (assuming a 2% fuel economy increase).

Results – additional GHG reduction with the use of the lubricating oil

The above section quantifies GHG savings during the manufacturing phase of the Altranex products. It has been documented by Lubrizol and reported in LubesNGreases magazine [12] that the use of lower viscosity, high-performance motor can increase fuel economy in motor vehicles by 2-4%. In fact, more GHG reduction can be achieved during its use phase, as the higher performance of the lubricating oil will lead to an increase in the fuel economy of the vehicles, which will result in the reduced fuel

consumption as well as the associated GHG emissions. (Table).

4 OTHER PRODUCTS

A co-product of the Altranex process is a renewable diesel, Altra-DZL. While the process is optimized to produce as much base oil as possible, under the operating conditions, approximately 10% of the end product is C17 hydrocarbons. This product has excellent cold weather properties and an energy content comparable to petroleum-based diesel and higher than biodiesel (FAME).

CHARACTERISTIC	TEST METHOD	Altra-DZL™
Density at 15°C kg/m ³	ISO 3675 or ISO 12185	827
Kinematic viscosity at 50°C mm ² /s (cSt)	ISO 3104	7.9
CCAI		750
Flashpoint, °C	ISO 2719	180
Acid number. mgKOH/g	ASTM D664	0.049
Pour point (upper), °C		-20
Water, % (V/V)	ISO 3733	0.1
Sulphur, % (m/m)	ISO 8754	<0.0001
Heat of Combustion (MJ/kg)	ISO 1716	45.564

Table 7: Typical properties of Altra-DZL

5 CONCLUSIONS

Altranex has developed an innovative process for producing hydrocarbons from renewable and waste feedstock. The key innovative step is an electrolysis that removes oxygen from fatty acids and simultaneously dimerizes them producing a hydrocarbon molecule that is ideal for lubricant and drop-in fuel applications. Altra-BASE shows promise as high-performance base oil that could replace synthetic (PAO) base oils with a lower-cost, higher VI alternative. Altranex is working in partnership with Valvoline to develop motor oils using Altra-BASE.

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