VALORISATION OF USED FRYING OILS AS NON-FOOD APPLICATIONS BY CATALYTIC TRANSESTERIFICATION

AVELLAN A.V., ALFOS C.

ITERG – French Institute for Fats and Oils – av.avellan@iterg.com

INTRODUCTION VALUIL is an European project dealing with a new valorisation of Used Frying Oils (UFO's) collected in Europe, as environmentally friendly biodegradable lubricants, intended to replace traditional mineral oils in applications such as loss oils (hydraulic fluids) and demoulding agents. The setting up of bio-lubricant bases from Used Frying Oils is carried out according to a catalytic transesterification process in presence of trimethylolpropane. This way leads to neopentylpolyol esters which present suitable properties in lubrication applications (low volatility, good thermic resistance, low flow point).

DISTRIBUTION OF THE EUROPEAN INDUSTRIAL PARTNERS IN VALUIL PROJECT

Upstream

OIL COLLECTORS
Sud Recuperation (F), Eurofat (B)
◊ UFO's collection
◊ Treatment

ITERG
Institute for Fats & Oils, France
◊ Study: variability of UFO's composition
◊ Chemical transformation (transesterification) at pilot scale

Downstream

LUBRICANT MANUFACTURERS
Natoil (D), Baraldi (I)
◊ Formulation tests
◊ Product evaluation study

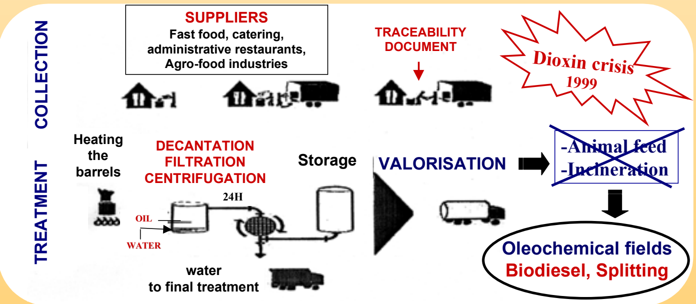
Final objective

◊ INDUSTRIAL TRANSFER
◊ ENVIRONMENTAL AND ECONOMIC VALIDATION

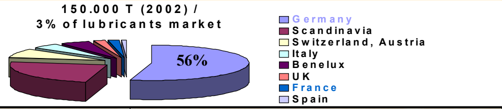
UFO's MARKET

EUROPEAN BIO-LUBRICANT MARKET

FRENCH COLLECTING ACTIVITY (France : 35 000 T / Europe : 350 000 T)



EUROPEAN DISTRIBUTION, BIO-LUBRICANT APPLICATION FIELDS AND THEIRS ECO-LABELS



APPLICATION FIELDS	ECO-LABELS
Hydraulic oils	Nordic Swan, Blue angel (D), Swedish Standard, VAMIL, ISO 15380
Chainsaw oils	Nordic Swan, Blue angel (D), NF-Environment Mark (Fr), Austrian eco-label
Gear oils	Nordic swan
Greases	Nordic Swan, Blue angel (D), Swedish Standard, VAMIL
Metalworking fluids	Nordic Swan
Mould oils/ Concrete release agents	Nordic Swan, Blue angel (D)
Two stroke oils	Nordic Swan

Compared to vegetable oils which present fluctuation prices, 0.7 to 1 €/kg during 2001 to 2003, UFO's show a constant cost around 0.3 €/kg included oil collection and treatment, which make them competitive on the market. The main drawback of this raw material lies in the variability of their chemical composition. Because of strict lubricant bases specifications, an extensive study (59 samples / 3 months) has been carried out concerning the variability of UFO's composition before the setting up of lubricant bases at laboratory scale.

STUDY OF USED FRYING OILS
Traceability and Characterisation

Two types of Used Frying Oils selected

Table 1 : UFO's characteristics

		MIXOIL	SEMI SOLID FAT
GC analysis: NF ISO 5508 / 5509 Fatty acid content (g/100g)		93.5	91.2
HPLC analysis / NF EN ISO 16931 Polymeric triglycerides %		5.7 (4.7 to 5.9)	8.2 (6.6 to 9.4)
NF EN ISO 8420 Polar compounds %		17.2 (22 to 25)	20.8 (> 25)
Oleic acidity % / NF ISO 660		4.4 (2.3 to 8.0)	2.4 (2.5 to 6.2)
Iodine value / NF ISO 3961		78 (73 to 79)	63 (60 to 68)
Sterol analysis (NF EN ISO 12228) and GC	Rapeseed	50%	8%
	Palm	30%	40%
	Tallow	20%	40%
	Sunflower	non identified	12%

Table 1 shows the presence of two different groups identified by sterol and fatty acid composition: mainly a majority of rapeseed origin for mixoil and tallow or palm for semi-solid fat.

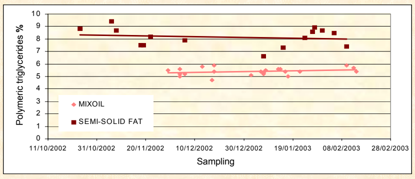
This difference is also noticeable by the iodine value (78 and 63), oleic acidity (4.4 and 2.4%) as well as the analysis of compounds formed during the deep frying process (180°C), namely polymeric triglycerides (5.7 and 8.2), polar compounds (majority of the samples between 22 and 25 % for Mixoil, above 25% for Semi-solid fat.

POLYMERIC TRIGLYCERIDES AND OLEIC ACIDITY VARIATION

Compared to refined oils as rapeseed and sunflower, the main difference in the chemical composition is due to the presence of polymeric triglycerides and a high acidity grade (storage conditions).

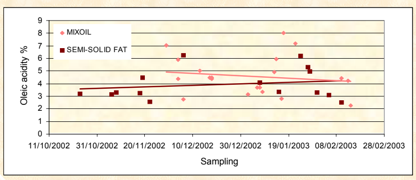
These parameters have been checked to see if these compounds could bring specific properties to bio-lubricants base synthesis.

✓ Polymeric triglycerides variation



- Non significant and similar variation
- Two different groups
- Control of polymeric triglycerides increase during the lubricant bases synthesis

✓ Oleic acidity variation

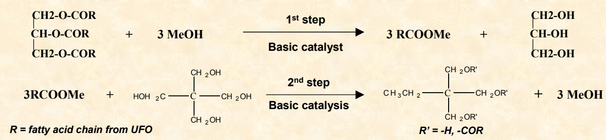


- Values higher than crude vegetable oils (~0.5 - 1%)
- Significant fluctuations for the two groups (storage conditions)
- Influence of acidity on the synthesis process of lubricant bases

BIO-LUBRICANT BASES
Synthesis and Results

Polyolesters synthesis is achieved by an integrated transesterification process in two steps : methanolysis of UFO's followed by a transesterification reaction in presence of trimethylolpropan (scheme 1).

Scheme 1 : polyolesters synthesis



DEMOULDING AGENT SPECIFICATIONS

Table 2 : Tested lubricant base specifications

Phys. and chem. Characteristics	Unit	Commercial lubricant base	Tested lubricant base
Chemical composition Acid value	%	TMP trioleate < 3.5	0.18
Appearance (20°C)	/	homogeneous, transparent liquid	Homogenous, Orange liquid
Viscosity (40°C)	cSt	70 - 95	46
Thermo-gravimetric analysis	Curve	/	Results included in the range
FTIR spectra	Spectra	/	Good match with the data

Table 2 presents results of a commercial product and a tested lubricant base which respond to the specifications set by the industrial partner as demoulding agent application. Similar behaviour of both products were observed of which acidity grade, below the expected value and the appearance of the sample, an orange homogenous liquid are important parameters.

A viscosity of 46 cst at 40°C were also obtained, close to the specifications. Then, the thermo-gravimetric analysis, specific to demoulding agent application is used to appreciate the thermo-oxidative stability of a sample. The results present a similar temperature decomposition and oxidative stability.

Finally, FTIR spectra show a fairly good match between both products concerning the main chemical function observed (free hydroxyl, ester function...). Tested lubricant base has been formulated in emulsion; it's stability is in progress and at the moment satisfying.

HYDRAULIC FLUID SPECIFICATIONS

Table 3: Tested lubricant base specifications

Phys.-chem. Characteristics	Unit	Commercial lubricant base	Tested lubricant base
Chemical composition Acid value Viscosity (40°C)	 % cst	Tallow TMP trioleate < 1 47	 0.18 46
Appearance (20°C)	/	liquid	homogeneous, orange liquid
Oxydative stability Rancimat induction period	h	0.4	3.6

Table 3 presents results of a commercial product and a tested lubricant base as hydraulic fluid application. The same remarks as table 2 can be made concerning the acid value, viscosity and the appearance of the sample.

The Rancimat test was carried out to appreciate the oxidative stability. The results show a better oxidative stability for the tested lubricant base (3.6 h) than the commercial one (0.4 h).

The lubricant base has been formulated as hydraulic fluid application (additives authorised for blue angel eco-label). Several tests are in progress.

CONCLUSION **The transformation of UFO's by catalytic transesterification has shown that the use of this raw material which presents a low variation range in it's composition, except acidity value, remains a promising route for the development of bio-lubricant bases. The next objective of VALUIL program aims the optimisation of the process in order to achieve the semi-industrial transfer on one hundred kilograms of raw material. The product performances are to be validate according to the different eco-labels specifications. Comparison of production cost between classical lubricant bases and these new derivatives are to be made.**