Reuse of waste animal fat in biodiesel: Biorefining heavily-degraded contaminant-rich waste animal fat and formulation as diesel fuel additive

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ABSTRACT

Here we report a study on the technical feasibility of using purified animal fat as additive in a diesel fuel for internal combustion engines. The objective is to obtain a base fat with contaminant-free and ready to be diluted in petroleum diesel to obtain a diesel fuel blend with acceptable characteristics in terms of engine-system tolerances.

A crude fat refining process composed of a vacuum distillation step and a glycerolysis step to convert the free fatty acids (FFA) recovered from distillation step into triglycerides (TAG) is used. Parametric study to determine the optimal purification-process conditions are used. The TAG obtained after a refining step, is then blended with standard diesel.

A satisfactory formulation has already been used to power a system-equipped (converted) diesel engine, and blend ratio of up to 40% in standard diesel perform well enough to run the target engine.

The results of this study show that this approach is technically feasible and economically interesting for recovering this waste into fuel. Moreover, it permits a decrease of the fuel carbon balance.

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1. Introduction

The food industry produces a lot of fatty effluents that is impossible to transform into a biodiesel due to high content of impurities and the acidity of the material. That's why; this high energetic byproduct is in the majority of cases eliminated in water treatment plant. Fortunately, we could see the development of new process like anaerobic digesters. So, in the best case, a local biogas installation could valorise the effluents into an energetic gas.

This article presents a new economical alternative to synthesize an additive which could be used in a standard diesel engine. This approach is completely new and offers a high treatment of a waste to recover it into fuel.

Depleting oilfield resources with increasingly tight oilfield extraction legislation is a big push factor for turning to new energy sources. Manufacturing biofuels from animal, plant or algal biomass feedstocks is one alternative to fossil fuels [1].

Animal fats are generally formed of a mixture of triglycerides TAG, proteins, water, and diverse minerals. A majority of fatty waste comes from urban sewage treatment, agrifood industries (casing processors, salt-curers, canners, slaughterhouses, dairies …), but also includes tallow and pork lard waste and restaurant grease trap waste. Animal by-products, which are sourced through the food—farming industry (the livestock value chain), slaughter-houses, butchers, and veterinary services, are the parts not intended for human consumption (fecal contents, manure, slurry, and fallen stock from farms). Bone, meat waste, fats and oils, and even feet material are reused in an array of process streams that can work with practically all the commodity stocks. In France, estimates for corporate cafeterias put the mean quantity of leftover waste at 250 g per meal, i.e. around 600,000 tons per year, to add to the 500,000 tons from retail restaurants [2]. The national stock of recoverable agrifood and restaurant-industry oil is an estimated 100,000 to 150,000 tons. However, estimates suggest only 25,000 tons gets collected annually, with the rest disposed of into drains and sewers or down kitchen sinks. Fat-oil-grease wastewater is produced at a rate of around 900 tons per day (200 g of waste per

meal) [3]. The food wastes that are rich on calcium like eggs shells, shrimp, mollusk and the waste frying oils can be catalysts of the biodiesel production process [4].

Fatty waste is qualified on the basis of its free fatty acid (FFA content), as either 'yellow grease' (<15%) or 'brown grease' (>15%). It is generally mostly composed of FFA, due to their advanced state of oxidation.

Free fatty acids, which are produced by degradation of fatty wastes, are characterized from chemistry and biochemistry points of view. Their melting point gets higher as chain length increases short-chain fatty acids are liquid at room temperature, whereas fatty acids with 10 or more carbon atoms are solid at room temperature.

Fatty acids can be split into two big families, called either saturated fatty acids when they have no double bonds or unsaturated fatty acids when they have 1 to 6 double bonds. Unsaturated fatty acids can be further prefixed as either monounsaturated when they have one double bond, or polyunsaturated when they have more than one double bond.

There are several industrially-viable techniques for reusing fat-oil-grease wastes. Some of the most widely practiced techniques are given below.

1.1. Composting

This is a fatty waste treatment that is carried out in mixture with a substrate (typically plant material or sawdust), generally using windrow or static-pile methods. Composting enables a 40% decrease in initial crude volume and a 30% reduction in moisture content, and a heat-hygienized final product. The process is also rainfall-sensitive, and the time required to afford a quality feedstock is relatively long.

1.2. Incineration

This method can treat fatty waste specifically or combined with household waste or sewage sludge. Fatty waste has to be pre-dehydrated due to its high-water content. Specifically incinerating fatty waste only requires around 20% dryness, and comes at a cost of high LHV (33,500−45,000 kJ/kg fat).

Fatty waste is relatively cheaper source than vegetable oil, making it a potential feedstock for biofuel. Biodiesel produced from fatty waste feedstocks from animal (or others vegetable oils and fat, frying oils) is considered non-toxic and biodegradable [5], which makes it a good substitute to diesel [6]. However, fatty waste is generally composed essentially of FFA, which does not only give it acid values over the engine-system tolerance limits (direct injection) but also precludes its conversion into biodiesel. For reuse in biofuel, the acid value has to be reduced at around $0.3g_{KOH}/g_{fat}$. In addition, animal fats contain very high amounts of fatty acids [7], sometimes going over the 90% mark. This over-acidic composition makes conversion into biodiesel difficult or even impossible via conventional base-catalyzed transesterification processes. A refining step is therefore necessary before they can potentially be reused in biofuel.

Biodiesel is defined as mono-alkyl esters of long-chain fatty acids derived from renewable feedstocks like vegetable oils, algal oils or animal fats, for use in compression-ignition (diesel) engines. It is considered a possible substitute or extender for standard diesel fuel and is generally considered as composed primarily of Fatty acid methyl ester FAME obtained from vegetable-oil triglycerides by transesterification with a short-chain alcohol, typically methanol. The resulting fuel is much like standard petroleum-derived diesel fuel in terms of key fuel characteristics, which means the two are compatible and can be blended in any proportions.

1.3. Pyrolysis

This method involves chemically modifying the fat molecules via a thermal process with air or nitrogen sparging. The pyrolysis of triglycerides has been a subject of intensive research to find a bio-based fuel adapted to diesel engines [8]. Studies have included the effect of temperature and type of catalyst on the conversion of triglycerides in order to obtain paraffins-oleins like those found in petrodiesel. The microwave co-pyrolysis was applied to the waste cooking and frying oil and waste polyolefins to convert them into biofuel [9,10]. The performing of the pyrolysis process in N_2 atmosphere and vacuum environment was examined [10].

1.4. Micro-emulsification

The emulsions are thermodynamically unstable dispersions of oil, water, and surfactant, often in combination with an amphiphilic molecule called co-surfactant [11−13]. The presence of surfactants and co-surfactants temporarily stabilizes this mixture of normally immiscible products. The droplets in the micro-emulsion vary in diameter from 100 to 1000 Å. The water content and sometimes alcohol content of the micro-emulsions means they have a lower heat of fuel combustion that diesel fuels. That said, it has been demonstrated that an emulsion fuel improves combustion, especially for very viscous fuel, and in terms of pollutant formation. The presence of water reduces the flash point, which means less NOx formation, and conjointly promotes puffing and micro-explosion events, which stops particulates forming [14].

1.5. Dilution (blending)

Animal fats and vegetable oils are blendable with solvents like ethanol or diesel fuels [15,16]. Kaufman et al [15] studied sunflower oil blended in a 1:3v/v ratio with diesel fuels and ran in-engine tests. The viscosity of the blend obtained was 4.88 cSt at 40 °C, prompting the authors to conclude that the blend was unsuitable for long-term use in direct-injection diesel engines due to severe coking of the injector nozzle. A comparable blend of high-oleic-acid safflower oil was also tested and gave satisfactory results, but long-term use was not an option as it thickened the lubricant, making it under-effective [17−19].

Transesterification: This chemical process consists in reacting the triglycerides with short-chain alcohols (typically ethanol or methanol) via acid-catalyzed or base-catalyzed (potassium hydroxide (KOH), sodium hydroxide (NaOH), or others) schemes [20]. If the catalyst is substrate-soluble, the process is called homogeneous catalysis; if not, it is called heterogeneous catalysis, as is the case with particulate bed reactors. Homogeneous catalysis processes are the more widely practiced in industry. However, the cost of treating the glycerol co-product and purifying the resulting biodiesel has prompted research to develop new more economical processes for cheaper yet better-quality biofuels. *Institut Français du Pétrole*—the French institute for petroleum science—has filed a patent proposing an animal or vegetable oil-based trans-esterification process driven by zinc, titanium or aluminium-based heterogeneous catalysts [21]. Note too that base catalysts are also widely used in the biodiesel industry because they carry little risk of engine corrosion.

In this study, we propose a waste fat biorefining strategy based on distillation separation of FFA and glycerolysis to convert FFA into TAG to produce a basic contaminant-free fat feedstock for use as a diesel fuel additive (less than 30% added) (Fig. 1).
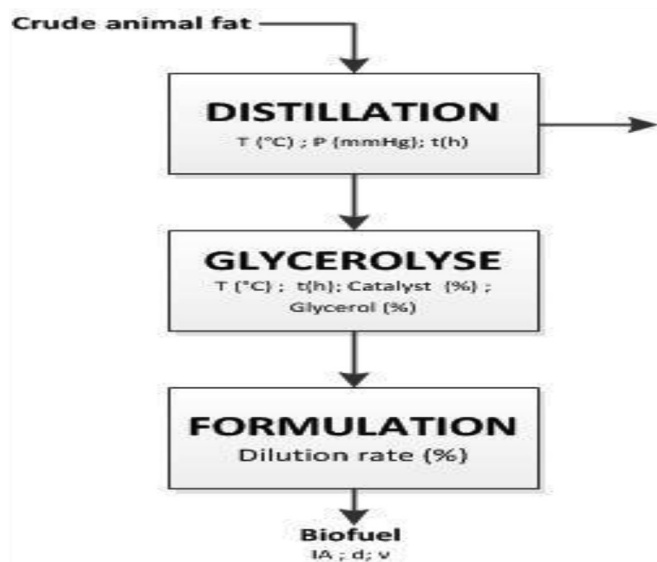
Fig. 1. Scheme for biorefining highly-degraded fatty wastes (schema proposed by S3D).

2. Materials and methods

2.1. Crude animal fat

The fatty waste used for this study (Fig. 2) is a highly-degraded base fat (>90% FFA) presenting a high acid value (150g_{KOH}/g_{fat}) that is vastly over the standard required for on-specification biodiesel (EN 14214), which sets 0.5 mg$_{KOH}$/g_{fat} as maximum permissible limit. Furthermore, this crude animal fat can contain contaminant levels of up to 1500 ppm, which is a logical consequence of its journey through the wastewater system. The lipid composition and physical–chemical properties of rendered animal fat are given in Table 1.

2.2. Distillation

The purpose of distillation is to remove the contaminants from the starting fat feedstock to recover a clean fat essentially composed of FFA. As the FFAs volatilize at a lower temperature than the TAG in the fat feedstock, the distillation process can recover the

Table 1
Composition of the crude animal fat.

Properties	Values
Acid value (mg$_{KOH}$/g_{fat})	150
Density	0.8
ν (m^2/s)	75 (55 °C)
FFA composition	52% saturated fatty acids
	20% monounsaturated fatty acids
	28% polyunsaturated fatty acids
% FFA	90%
% TAG	10%
Contaminants	1500 ppm

FFA in the distillate and the TAG in the residue. The TAG residue is like bitumen (polymerization), which could be recycled as a by-product via direct combustion. The two recovered fractions are then investigated by contaminant analysis to determine their separation yields. A pressure/temperature parametric study is then performed to determine the optimal distillation conditions for the crude fat feedstock. Literature on the distillation of animal fat is rare, but certain authors advocate distillation at temperatures between 200 and 270 °C and pressures between 5 and 25 mmHg depending on source-fat composition [22–24]. Temperature and pressure are the critical distillation unit operation parameters. However, 270 °C is a maximum temperature, because as soon as process temperature creeps over 270 °C, the reactive medium becomes exothermic, and thermal runaway leads to thermal cracking of the fat— a destructive thermochemical process that breaks down the fat to form heavy hydrocarbons and gases. The use of an inert gas—in this case nitrogen—as stripping gas to facilitate the FFA separation process has also been recommended [25–27]. In this study, a pressure range between 13 and 20 mmHg was studied for a set-point heating temperature of 260 °C in line with the literature data. Experiments were led at pilot scale.

2.3. Esterification of FFA into TAG (glycerolysis)

The purpose of glycerolysis is to convert the FFA distillate into mono-, di- and triglycerides in order to bring its acidity down to a minimum [28]. Glycerolysis is an esterification reaction between glycerol (a trihydric alcohol) and FFA that leads to the formation of mono-, di- and triglycerides (Fig. 3).

We led a parametric study of the influence of various key process parameters on the glycerolysis reaction, *i.e.* type of catalyst, amount of catalyst, percentage of surplus glycerol relative to the reaction stoichiometry (Fig. 3), temperature, and reaction time (Table 2).

In all the test, we used a 20 g mass of fat. Amount of glycerol was calculated from the reaction following equation (1) according to stoichiometry of the reaction:
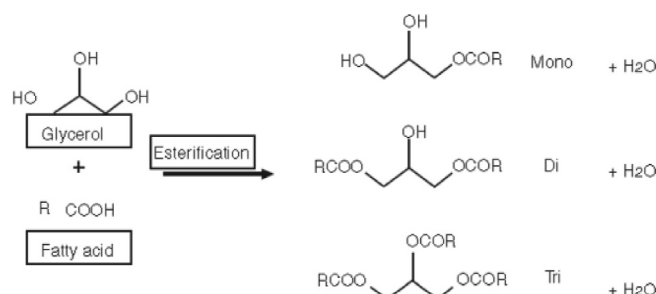

Fig. 2. Crude animal fat.

Fig. 3. Glycerolysis reaction equation.

Table 2
Parametric study of the glycerolysis process.

	Parameters	Values
Catalysts:	Type	zinc acetate
		zinc sulfate
		potassium hydroxide
		magnesium oxide
	% (w/w)/fat	0.5%, 1%, and 1.5%
Surplus glycerol	% (w/w)/fat	5%, 12.5%, 20%, and 30%
Temperature		220 °C and 230 °C
Reaction time		max = 4.5 h

$$m_{Gly} = \frac{1}{3} m_{FFA} \frac{M_{Gly}}{M_{FFA}} \tag{1}$$

where $m_{Gly}(g)$ and $M_{Gly}(\frac{g}{mol})$ are mass and molar mass of glycerol, respectively, and $m_{FFA}(g)$ and $M_{FFA}(\frac{g}{mol})$ are mass and molar mass of FFA, respectively.

The mean molar mass of the cleaned fat used, M_{FFA}, calculated based on the lipid composition of the starting fat feedstock, was 260 g/mol. Mass of catalyst was initially set at 1 wt% relative to mass of fat, and temperature was initially set at 220 °C for all tests. These parameters were then optimized in response to the first results obtained. Stoichiometric quantity of glycerol, calculated from the reaction equation given in Fig. 3, was 12% of the mass of fat used. Glycerolysis reaction kinetics was monitored by measuring the reaction−course decrease in acid value.

2.4. Dilution (blending)

Here we studied conditions for blending the purified fat in standard diesel. TGA from glycerolysis reaction was added with diesel to form a mixt at different proportion [10%−40%] by weight. The properties of the biofuels obtained were then analyzed to be compared against standard diesel and against European standard EN 14214 on biodiesel [29]. This analysis focused primarily on kinematic viscosity, carboxylic acid content and density.

3. Results and discussion

3.1. Distillation

Distillation process time, at a given pressure, is influenced by heating rate. Here we evaluated the unit-process operation time, defined as time from first droplet of distillate to entirely completed distillation, i.e. 45−60 min. Once this operation was completed, we recovered a clean (distillate) white-colored fat, as illustrated in Fig. 4. The operating conditions (Table 3) for distillation to selectively yield a maximum amount of clean fat were a max temperature of 260 °C and a process pressure of 13−14 mmHg. The amount of distillate recovered increased with decreasing process pressure. However, temperature is capped at 270−280 °C, because as soon as process temperature creeps over these values, the fat can get thermally cracked by destructive chemical breakdown. All the distillate acid values obtained were greater than or practically equal to 200 mg$_{KOH}$/g$_{fat}$, which correspond to a clean fat essentially composed of FFA. To get a better understanding of the fat distillation process, chromatography would be useful to identify the different phases recovered as a function of headspace vapor temperature, and thus learn what type of fat is recovered as a function of process temperature.

The lab-scale results obtained here enabled us to achieve relatively low yields (53%), and extrapolation up to pilot-plant scale found that better results are afforded by a 75% increase in

Fig. 4. Fat recovered in the column overhead at the distillation step.

separation yield. We thus used a pilot-scale distillation set-up to perform FFA separation with a volume of 1000 kg of crude fat heated up to 260 °C under a pressure set low enough to hold the mixture in liquid phase. A flash separation step at a reduced pressure of 4 mmHg was able to volatilize and then re-condense practically all the FFA. Flash distillation afforded FFA at 75% higher recovery rates than at lab scale. These process conditions were not reproducible at lab scale, due to safety concerns.

Here, then, at pilot scale, the optimal conditions found for input volumes of around 1 m^3 were a temperature of 270 °C and pressure of 4 mmHg. Under these conditions, we obtained a distillation yield approaching the 75% mark. The 25% of essentially TAG residues, which are difficult to recover under the optimal conditions here, could be recycled via combustion.

3.1.1. Contaminant analysis

The determination of total contamination here is compatible with standard EN 12662 (analytical method). Contaminant analysis was carried out on the distillate and on the residue, and the results are given in Table 4:

Results of analysis on both distillate and residue showed that after distillation, the contaminants initially present in the crude animal fat end up trapped in the residue, thus enabling to recover a practically contaminant-free fat in the distillate (Table 4). Total amount of contaminants found in the distillate is lower than the maximum amount required under the current biodiesel standard specifications.

3.2. Glycerolysis

Results for the glycerolysis step to convert the FFA recovered into triglycerides are reported in Table 5 (reactions without catalyst) and Table 6 (reactions with catalyst).

Analysis on test-runs without catalyst showed a reduction in acid value from 200 down 26.92 mg$_{KOH}$/g$_{fat}$, which equates to a FFA-to-TAG conversion yield of around 86%. However, this acid value is still high and fails to meet the characteristics required for biofuel blends applied in standard fuel diesel engines. Note too that analysis on test-runs with catalyst showed substantially higher conversion yields with relatively low acid values, especially with

Table 3
Test-by-test results of the distillation step.

Test #	Input (g)	T (°C)	P (mmHg)	Distillate (g)	AV (mg$_{KOH}$ /g$_{fat}$)	yield (%)
1	153	250	20	19.6	201	13
2	224	250	15	39	209	17
3	236	260	20	66.92	196	28
4	250	260	15	83.3	211.5	33
5	269	250	14	121	213	45
6	356	260	15	161.63	213	45
7	320	260	14	171.15	209	53
Pilot scale	1000 kg	270	4	750 kg	200	75

Table 4
Contaminant analysis in the distillate and in the residue.

Contaminants	Distillate	Residue
Total phosphorus (mg/kg) — dry	<2.5	2290
Calcium (mg/kg) — dry	<4	9000
Magnesium (mg/kg) — dry	<1	340
Sodium (mg/kg) — dry	<2	210
Potassium (mg/kg) — dry	8	80
Silicon (mg/kg) — dry	<1	<1
Dry matter (mg/kg)	93.5	98.85

Table 5
Results of the study investigating the glycerolysis reaction: without catalyst.

Viscosity at 40 °C (Pa·s)	0.16	0.07
% surplus glycerol	**5.00**	20.00
AV (mg$_{KOH}$/g)	ND	26.92
% reduction of FFA	ND	85.75

zinc sulfate as catalyst (AV ~ 5.6 mg$_{KOH}$ /g$_{fat}$). The final fat obtained after glycerolysis reaction have a dark-brown color.

A temperature of 260 °C, under a low pressure of 14 mmHg, enabled a post-distillation recovery of over 75% of the initial input. In addition, distillate and residue fraction analysis showed that the contaminants initially present in the crude fat (1500 ppm) is reduced to traces. Furthermore, the FFAs thus obtained were converted into TAG by a glycerolysis reaction at 220 °C for 4 h in the presence of a zinc sulfate catalyst. This unit operation reduces the acid value of the fat below 7 mg$_{KOH}$ /g$_{fat}$ and the measured viscosity down to less than 9 cSt, thus meeting the current standards of diesel fuel.

3.3. Dilution

The fat derived from the glycerolysis step was tested in different formulations corresponding to 10, 20, 30 and 40% (w/w) post-

glycerolysis fat in standard diesel. The results obtained are reported in Table 7. The properties of the biofuels obtained were then analyzed to be compared against standard diesel and against European standard EN 14214 on biodiesel [16]. This analysis focused primarily on kinematic viscosity, carboxylic acid content, and density. The results obtained are reported in Table 7.

Both the density and kinematic viscosity of the fuels blended are comparable to those of standard biodiesel. In comparison with vegetable oils, which are occasionally used directly as biofuels, the blends we put together here —even up to 40%— demonstrate characteristics that are closer to those of biodiesels produced by transesterification according to standard EN 14214.

The next step in this project is to characterize the various formulations put together here according to the biodiesel standard (LHV, HHV, cloud point, cold filter plugging point (winter), cetane number and flash point) before proceeding with in-engine tests.

4. Conclusions

This study found the process parameters needed to feasibly meet the objectives that we had set out at the start, *i.e.*

- To synthesize a clean, contaminant-free fat feedstock presenting a low acid value.
- Distillation up to a maximum process temperature of 260 °C at a pressure in the 13—14 mmHg, bracket affords a clean fat with a 75% yield at pilot scale.
- Distillation cuts total contaminants down to a value of less than 20 ppm, which is well below the 24 ppm value set by standard EN 14214.
- The use of zinc sulfate as catalyst at 1% (w/w) relative to mass of fat, with 5% surplus glycerol relative to the reaction stoichiometry and a process temperature of 220 °C for 4 h, brings the acid value down by 96% of its initial value, i.e. down to a final acid value approaching 6 mg$_{KOH}$/g$_{fat}$. Note that the fat obtained has a melting point of between 32 °C and 33 °C.

Table 6
Results of the study investigating the glycerolysis reaction: with catalyst.

Catalyst	Surplus glycerol (%)	FFA reduction (%)	viscosity at 40°C (Pa·s)	AV (mg$_{KOH}$/g)
Zinc	5.0	92.30	ND	14.63
	12.5	90.74	ND	17.73
	20.0	94.30	0.06	11.00
	30.0	95.06	0.07	9.63
Zinc sulfate	5.0	97.04	0.10	5.63
	12.5	90.57	ND	18.06
	20.0	89.79	0.05	19.72
	30.0	95.06	0.07	9.63
Zinc acetate	5.0	92.06	0.11	15.18
	12.5	94.61	0.07	10.32
	20.0	94.41	0.06	10.79
	30.0	83.59	ND	32.11

Table 7
Different blend ratios of the biorefined fat in standard diesel.

Dilution rate (%)	Kinematic viscosity at 40°C (mm^2/s)	Density (−)	Acid value calculated (mg$_{KOH}$/g)
10	1.81 ± 0.01	0.831	0.7
20	3.12 ± 0.02	0.837	1.4
30	5.18 ± 0.01	0.847	2.31
40	6.53 ± 0.15	0.855	2.98
Standard diesel fuel (EN 590)	[2–4.5]	[0.820–0.845]	−
Biodiesel (EN 14214)	[3.5–5]	[0.86–0.90]	max = 0.5
Vegetable oil	>20	[0.90–0.95]	−

After glycerolysis, 10% and 20% dilutions of the fat obtained blended in standard diesel meet the standard specifications on kinematic viscosity and density. However, the corresponding acid values are still higher than the on-specification acid value of standard diesel according to EN 14214. The use of an acid absorber offers a way to reduce these values and brings the biofuel produced down to a more acceptable level in terms of engine-system tolerances.
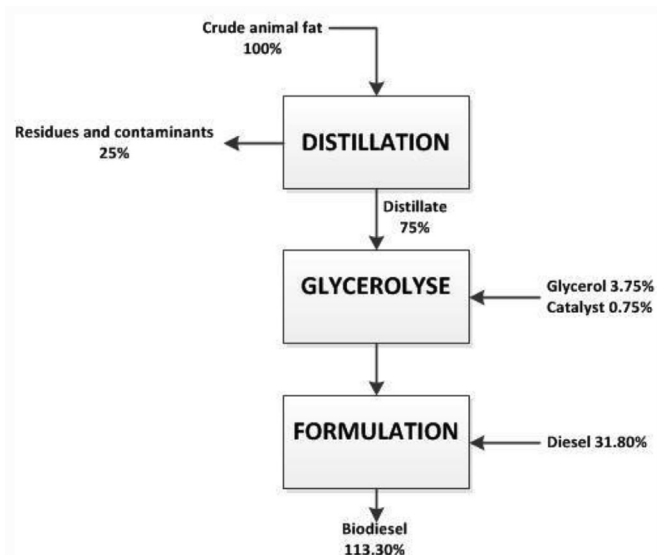
The final diesel fuel obtained, after blending, meets current diesel fuel standards parameters (kinematic viscosity between, 2.00–4.50 mm^2/s at 40 °C, pH, between 5.5 and 8, and its lower heating value, PCI of the order of 44.8 MJ/kg according to standards International NF EN 590 and ASTM D975-18).

The mass balance of the different component unit steps is reported in Fig. 5. This mass balance was obtained with the pilot-scale distillation yield (75% of FFA recovered). The total amount of biodiesel obtained with a 40% dilution in standard diesel corresponds to 113% of the amount of crude fat converted.

Nowadays a biodiesel plant is used to produce fuel mainly based on vegetable oil. Several innovative processes permit to valorise used cooking oil but the proportion of this raw material in the process remains low. In all cases, the different companies have to pay the raw material in order to feed their processes, that's why the common biodiesel unit treats 100,000 tons per year to reach an economic threshold. With our process, the raw material has a negative price and then in that case, the economic threshold is easily reached. The advantage is to be able to valorise very bad quality fat which is considered as a waste by the industrial community.

Fig. 5. Net mass balance of the process.

References

[1] O. Andersen, J.E. Weinbach, Residual animal fat and fish for biodiesel production. Potentials in Norway, Biomass Bioenergy 34 (8) (2010) 1183–1188.

[2] ADEME report: Les déchets alimentaires premiers pas vers la réduction et la valorisation, 2011.

[3] ADEME Report: Etude De La Gestion De La Filiere De Collecte Et De Valorisation Des Huiles Usagees Dans Certains Pays De L ' Ue, 2010.

[4] M. Catarino, M. Ramos, A.P. Soares Dias, M.T. Santos, J.F. Puna, J.F. Gomes, Calcium rich food wastes based catalysts for biodiesel production, Waste Biomass Valoriz. 8 (5) (2017) 1699–1707.

[5] C. Jammes, Co-valorisation d'effluents graisseux et de résidus lignocellulosiques: déshydratation mécanique et compostage, Thèse de doctorat, Université de Limoges,Faculté des sciences et techniques, 2007.

[6] M. Canakci, J. Van Gerpen, Biodiesel production from oils and fats with high free fatty acids, Trans. Soc. Agric. Eng. 44 (6) (2001) 1429–1436.

[7] J.M. Encinar, N. Sánchez, G. Martínez, L. García, Study of biodiesel production from animal fats with high free fatty acid content, Bioresour. Technol. 102 (23) (2011) 10907–10914.

[8] K.D. Maher, D.C. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresour. Technol. 98 (12) (2007) 2351–2368.

[9] S.S. Lam, W.A. Wan Mahari, A. Jusoh, C.T. Chong, C.L. Lee, H.A. Chase, Pyrolysis using microwave absorbents as reaction bed: an improved approach to transform used frying oil into biofuel product with desirable properties, J. Clean. Prod. 147 (2017) 263–272.

[10] W.A. Wan Mahari, C.T. Chong, W.H. Lam, T.N.S.T. Anuar, N.L. Ma, M.D. Ibrahim, S.S. Lam, Microwave co-pyrolysis of waste polyolefins and waste cooking oil: influence of N2 atmosphere versus vacuum environment, Energy Convers. Manag. 171 (2018) 1292–1301.

[11] A. Kerihuel, M.S. Kumar, J. Bellettre, M. Tazerout, Use of animal fats as CI engine fuel by making stable emulsions with water and methanol, Fuel 84 (12) (2005) 1713–1716.

[12] M.S. Kumar, A. Kerihuel, J. Bellettre, M. Tazerout, Experimental investigations on the use of preheated animal fat as fuel in a compression ignition engine, Renew. Energy 30 (9) (2005) 1443–1456.

[13] A. Kerihuel, M.S. Kumar, J. Bellettre, M. Tazerout, Ethanol animal fat emulsions as a diesel engine fuel–Part 1: formulations and influential parameters, Fuel 85 (17) (2006) 2640–2645.

[14] A. Kerihuel, Etude de la formulation et de la combustion de carburants alternatifs à base de graisses animales pour moteur à allumage spontané, Thèse de doctorat.Université de Nantes, 2007.

[15] K.R. Kaufman, M. Ziejewski, Sunflower methyl esters for direct injected diesel engines, Trans. ASAE. 27 (6) (1984) 1626–1633.

[16] J.W. Goodrum, D.P. Geller, T.T. Adams, Rheological characterization of animal fats and their mixtures with #2 fuel oil, Biomass Bioenergy 24 (3) (2003) 249–256.

[17] T. Eryilmaz, M.K. Yesilyurt, Influence of blending ratio on the physicochemical properties of saf fl ower oil methyl ester-saf fl ower oil , saf fl ower oil methyl ester- diesel and saf fl ower oil-diesel, Renew. Energy 95 (2016) 233–247.

[18] C. Valcir, R.F. Santos, J. Antonio, R. Aparecido, N. Barchinski, G. Salmazo, L.K. Tokura, F.F. Klajn, Industrial Crops & Products Chemical characterization of oil and biodiesel from four safflower genotypes, Ind. Crops Prod. 123 (2018) 192–196.

[19] H. Bateni, F. Bateni, C. Able, M.S. Noori, Biorefinery of safflower seeds in a sequential process for effective use of the substrate for biofuel production, Waste Biomass Valoriz. 9 (11) (2017) 2145–2155.

[20] J.M. Encinar, J.F. González, A. Rodríguez-Reinares, Ethanolysis of used frying oil. Biodiesel preparation and characterization, Fuel Process. Technol. 88 (5) (2007) 513–522.

[21] Acakpo, G., Delfort, B., Hillion, G., Lacome, T., Leporcq, S., Revel, R.: Process for the transesterification of plant and animal oils using heterogenous catalyst based on Titanium, zirconium, or antimony with aluminium. Google Patents (2005).

[22] K.S. Rhee, Minimization of further lipid peroxidation in the distillation 2-thiobarbituric acid test of fish and meat, J. Food Sci. 43 (6) (1978) 1776–1778.

[23] À. Oterhals, B. Kvamme, M.H.G. Berntssen, Modeling of a short-path distillation process to remove persistent organic pollutants in fish oil based on process parameters and quantitative structure properties relationships,

Chemosphere 80 (2) (2010) 83–92.

[24] P.J. Watkins, G. Rose, R.D. Warner, F.R. Dunshea, D.W. Pethick, A comparison of solid-phase microextraction (SPME) with simultaneous distillation-extraction (SDE) for the analysis of volatile compounds in heated beef and sheep fats, Meat Sci. 91 (2) (2012) 99–107.

[25] E.G. Constante, F.R. Berbel, A.P. Torronteras, J.H. Lope, Deacidification by distillation using nitrogen as stripper. Possible application to the refining of edible fats, Grasas Aceites 42 (4) (1991) 286–292.

[26] E.G. Constante, J.B. Gancedo, F.R. Berbel, M.V. Ruíz-Méndez, Physical refining of edible oils using nitrogen as stripping gas. Process optimization, Grasas Aceites 45 (3) (1994) 132–146.

[27] P.F. Martins, V.M. Ito, C.B. Batistella, M.W. Maciel, Free fatty acid separation from vegetable oil deodorizer distillate using molecular distillation process, Sep. Purif. Technol. 48 (1) (2006) 78–84.

[28] P. Felizardo, J. Machado, D. Vergueiro, M.J.N. Correia, J.P. Gomes, J.M. Bordado, Study on the glycerolysis reaction of high free fatty acid oils for use as bio-diesel feedstock, Fuel Process. Technol. 92 (6) (2011) 1225–1229.

[29] M. Berrios, M.C. Gutierrez, M.A. Martin, A. Martin, Obtaining biodiesel from Spanish used frying oil: issues in meeting the EN 14214 biodiesel standard, Biomass Bioenergy 34 (3) (2010) 312–318.