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Technological Aspects of Refuse Fats, Pretreatment and Retrofitting

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Abstract: Scope of the article is to discuss pretreatment of refuse, nonedible animal fats into biodiesel feedstock to improve yields of standard quality biofuel at low operational costs. Recommendations are equally viable for 2nd generation biodiesel processing technologies and to extend catalysts lifetime. Refuse fats are vulnerability to storage conditions having significant influence on loss of market value. Common concerns expressed in terms of high levels of FFA (Free Fatty Acid), moisture, impurities have been addressed. Detrimental constituents are present in these feedstocks in complicated, stubborn colloid chemical structures with direct impacts on processing. Common edible grade oil techniques have been revisited but failed to produce high market-value biodiesel feedstock at acceptable levels of yield and reliability. Petroleum refinery techniques, selective solvent refining and vacuum distillation have also not met expectations. Glycerolysis and direct esterification conversion techniques were efficient in reduction of FFA and impurities to acceptably low level at reasonable yield. Acid catalyzed direct esterification proved to be lower cost technique to produce good quality biodiesel feedstock that can be processed in first generation alkali-based transesterification and hydrotreatment techniques alike. Co-Sol apolar solvent born technology has been shown to be the best performing option in retrofitting. Direct esterification was demonstrated in a truly continuous, counter current, solvent born mode with substantial energy and resource efficiency gains.

Key words: Waste to fuel, renewable energy, biodiesel, resource efficiency.

1. Introduction

Pioneering work of Koerbitz [1] demonstrated that the price of feedstock is the single most important element in feasibility of biodiesel processing. It can represent close to 80% of OPEX (Operational Expenses). Least expensive feedstock processing has been in forefront of biodiesel development efforts for profit. However, reprocessing a biodiesel product that fails to fully meet standard criteria (called off-spec) can have double negative impact. It must be reprocessed on the expense of withholding normal operational capacities at additional OPEX. The use of inexpensive feedstock has been a leitmotiv to any generation technologies, for conventional alkali transesterification techniques and high pressure catalytic hydrotreatment conversion operations. Common concerns relate to high levels of FFA (Free Fatty Acid), moisture, impurities in the form of complicated, stubborn colloid chemical features. Most treaties address the matter of FFA content as primary criteria. We have accepted this widely-held assumption that FFA can be an important signal consideration.

For the hunt for such inexpensive feedstock other selected quality parameters should be considered for ecological and sustainability issues. The most commonly cited “*food or fuel”* dilemma is for sure a way of asking for resource and energy efficiency. But, for a more adequate imperative to social wellbeing, to environmentally conscious consumption we have asked for “*food and then fuel*” [2]. This way of multiple use of food has historically provided more

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feedstock for multi-feedstock biodiesel processing and has also made possible to adapt practices to schemes that support circular economy.

Processing refuse stocks of the scope of this work posed not only technological and economic barriers but legal alike. Statistics clearly show that the lowest price biodiesel feedstocks come from refuse sources. Yellow, brown grease and animal fat are the general terms for those sources that cannot be processed to food and related commodities but just into fuels for energy generation. Yellow and brown greases are the terms used in the USA. Rendered, nonedible animal fats are the terms in Europe, which are categorized by EU Regulation [3] as follows:

Category 3 has properties close to specific parameters of edible fats, but cannot be used in human consumption because of commercial, esthetic or hygienic reasons but they can be easily processed into animal feed and cosmetic compositions.

Category 2 is also high-risk, including fallen stock, manure and digestive content. Cat. 2 is also the default status of any material that does not fall into Cat. 1 or 3. In addition to the Cat. 1 fats, Cat. 2 material may also be used as organic fertilizer and soil improvers and can be composted or anaerobically digested.

Category 1 has the highest risk of spreading disease such as bovine spongiform encephalopathy, known as BSE and includes the bovine spinal cord, pet animals, zoo and circus animals, wild animals suspected of carrying a disease, and catering waste from international transport. Cat. 1 material needs to be disposed of, either by incineration or as a fuel for combustion. If treated correctly, it can be landfilled.

Having in stock fats from different sources, the mix must be classified according to the lowest category component, whatever is the provenance and extent, because the lower risk category material is contaminated by the highest risk components. Fats of Category 3 are outside the scope of our work. We have dealt with treatment of fats of Categories 1 and 2, originated in collection and rendering system of fallen animals by ATEV ZRt, a state owned company, responsible for country-wide collection and treatment. It has been beneficiary of the work.

The RED (Renewable Energy Directive 2009/28/CE) [4] states that waste-based biofuels can be counted twice in the calculation of the shares of renewable energy in transportation fuels. Categories 1 and 2 fats qualify for premium, double counting in emissions compliance if converted to biofuels. We would argue that the market for refuse fuels is, fundamentally, demand lead. However, this double counting has the effect of creating the conditions of a supply lead market with analysts predicting, rapid, high-growth in the value of transactions. The amount of fats available to biodiesel processing at EU level is 0.5-0.7 million tons/y. The amount of refuse fats of Categories 1 and 2 processed by the company is close to 10 thousand tons/y. It is an important message: proper processing technologies should fall in the scale of small to medium size operation.

Historic worldwide supply characteristics show close to 6 million m^3 refuse stock sold for biodiesel processing at a selling price of less than 0.25 EUR/kg [5, 6]. More recent transactions show that the price of refuse fats has climbed slightly above this level. For the sake of comparison, the average cost of rapeseed oil used in 1st generation units is between 800-900 EUR/t.

Biodiesel feedstock demands have been changed in favor of such refuse biodiesel feedstock at the expense of edible oil sources because of economic and legislative reasons. Demand characteristics have been biased by technology constraints due to conversion problems associated of this type of feedstock. Profitably criteria in converting inexpensive, but difficult to process feedstocks resulted in substantial closure and lay idle of 1st generation small and medium capacity units in Europe. It is to bear in mind that demand characteristics have been affected by preponderance of high capacity hydro-diesel units. The appetite for economic feedstocks has been limited by the extent of impurities, because contaminants pose risk to catalysts by deactivation of active sites. A reason why economy to scale of hydro-diesel processing is higher by an order of magnitude than that of second generation, methyl-ester producing units is that even after partial deactivation reserve activity should produce good quality fuel without replenishing the catalyst bed.

Scope of the exercise was to recommend feasible schemes for refuse stock pretreatment that conserve resources and avoid spending excessive cost for retrofitting. Direct beneficiaries of the work are small and medium size biodiesel processors that can not afford to employ high pressure, high throughput techniques that are favored by large capacity processing technologies. Improved efficiency has been approached in terms of avoided losses, through higher yields of biodiesel. Recommendations should be equally viable to 1st and higher generation technologies alike.

1.1 State of the Art of Processing

Biodiesel processing has been mostly viewed as transesterification of refined rapeseed, soy and palm oil. Glycerol component of a TG (Triglyceride) was substituted by methanol. The refined vegetable oil, that is mainly a composition of esters of different glycerol-fatty acids, is split into FAME (Fatty Acid Methyl Esters) and glycerol in alkali catalyzed reversible reaction (see Fig. 1). This is an over-simplification of a rather complicated sequence of operations especially when the feedstock consists or contains refuse sources. Inexpensive feedstocks contain different impurities in difficult to handle colloid systems. Most of the treaties approach the problem by discussing the presence of significant amounts of FFA. FFAs are generated in handling, storage and use. Thermochemical degradation reactions lead to even lower quality. Depending on FFA and other impurities contents, losses can build up to 15-50% of the feedstock in overall biodiesel processing routes. FFAs constitute the major element that determinates losses, depending on amount and complexity of colloid structure. In 1st generation technologies soap formation with caustic catalyst is the most rapid chemical reaction. It consumes the catalyst with release of water and freezes all desired reactions. Presence of water and shear conditions make difficult to tackle stubborn dispersions.

Intermediary trans-esterification products MG/DG (Mono- and Di-Glycerides) are also efficient surface active agents and do act to promote development of more complex emulsions. This is a reason why most of published works have focused on reduction of FFA. It has been accepted that an FFA level of less than 1% can be efficiently processed by trans-esterification with alkaline catalyst to standard fuel-grade biodiesel. Pioneering article of Canacki and Gerpen [7], written almost 20 years ago has been cited for more than 1,000 times. In this work synthetic brown grease, with

$$FFA + KOH \overset{\square\square}{\Longleftrightarrow\!\gg} FFK + H_2O \quad ❶ \text{ (saponification)}$$

$$FFA + CH_3OH \overset{\square\square}{\Longleftrightarrow} FAME + H_2O \quad ❷ \text{ (esterification)}$$

$$TG + CH_3OH \overset{\square\square}{\Longleftrightarrow} FAME + DG \quad ❸ \text{ (transesterification, step-1)}$$

$$DG + CH_3OH \overset{\square\square}{\Longleftrightarrow} FAME + MG \quad ❹ \text{ (transesterification, step-2)}$$

$$MG + CH_3OH \overset{\square\square}{\Longleftrightarrow} FAME + G \quad ❺ \text{ (transesterification, step-3)}$$

$$Impurities + CH_3OH \overset{\square\square}{\Longleftrightarrow} [G - phase] \quad ❻ \text{ (extractive refining)}$$

Fig. 1 Basic reactions in a first generation biodiesel technology. (TG: tri-glyceride, DG: di-glyceride, MG: mono-glyceride, G: glycerol, FAME: fatty acid methyl ester). It is adamant to understand the reversible character of these reactions leading to equilibrium, even in the case of separation of impurities.

33% FFA level, was treated to reduce the acid level to less than 1% and processed to standard fuel-grade biodiesel. The weak point was that palmitic acid was added as FFA model compound to refined vegetable oil. Colloid characteristics of the substrate were different than that of real systems. High rates of specific use of catalysts and reagents resulted in yields below 75%, i.e. a fourth of the feedstock has been wasted. It is to acknowledge that later studies and process developments have observed recommendations of Canacki and Gerpen.

Experts in the field may ask if these recommendations have been observed and considered for 20 years, is it worth for reporting? We dare saying YES! An accepted paper with the statement of "the addition of hexane as a co-solvent facilitated the miscibility of the oil in glycerol and improved the glycerolysis reaction efficiency" [8] provoked this reaction. This statement is false on physical chemistry basis! Hexane co-solvent does improve efficiency of trans-esterification and biodiesel processes as our patent was granted in 2009 [9]. The statement is false, apolar hexane does not dissolve glycerol and glycerol does not dissolve hexane [10]. We explain how hexane addition does improve efficiency in real.

There are reported figures of losses in yield related to high FFA, but are not fully convincing [11]. Yield levels vary in a range of 60-88%, i.e. the loss is between 12-40%. It is an economic point in assessing trade characteristics of refuse biodiesel feedstock. It has been accepted that MIU level should not be higher than 5%, whatever the level of FFA was. The term of MIU relates to moisture content: M, insoluble: I and unsaponifiable: U, mostly expressed in %. For ideal performance of biodiesel processing it is to regard MIU with relevance feedstock selection. M and I can not be converted to biodiesel and they end up in the polar, glycerine phase (G-phase). U, is mostly collected in the apolar biodiesel phase. If all FFAs are converted to FAME, by whatever technique, as discussed in the experimental section, the target yield value should be close to $Y = 100 - (I + M)$ [%]. It is evident that the higher the I and M, the higher the loss of insoluble and mechanical impurities that are made up by plastic wrapping sheets and debris, animal carcass and protein components. Low aesthetic value and odour of the stocks are additional annoyances. If only I and M would determine yield, the yield in the referred article would have been close to 100%. The reason to lose significant amount of resources indicates that not only feedstock characteristics, but operational procedures have definite influence on yield, hence on profitability.

In response to the provoking article, we dared to extend reactions involved in 1th generation technologies with extractive refining, an action exerted by the byproduct glycerol (reaction 6). In terms of unit operations, phase separation into apolar fuel and polar glycerol phases (G-phase) is a selective solvent refining. This difficult operation is very much influenced by colloid chemical phenomena, leading to a reversible equilibrium colloid system. This requires specific attention and expertise in operation, especially under real-world conditions. Further, if apolar FFAs collect in the polar phase in the form of FAK, valuable amount of feedstock components ends in the waste pool. For efficient operation FFAs must be recycled!

Reported efforts in processing refuse stocks to biodiesel feedstock have discussed techniques mostly based on expertise in processing edible oil. These are: water washing—a unit operation of solvent extraction, neutralization, degumming, both connected to water washing, bleaching, vacuum distillation and drying. Most studied pretreatment methods combine neutralization, degumming, alkali refining, adsorption and bleaching with acid and odor removals by the use of vacuum distillation or by the use of membrane processes. These typical conventional techniques remove FFA, phosphatides, known as gum, and other impurities. A number of different impurities that are not present in edible oil or rendered fat may act as stabilizers in difficult to handle refuse stocks.

1.2 Common Treatment Techniques

1.2.1 Neutralization Pretreatment

The feedstock is contacted with an alkali, or alkali containing stream to convert FFA into soap and the soap containing water phase is separated from the supernatant oil phase reduced in FFA level. In selected first generation technologies this is cleverly (?) done by contacting the feedstock with the highly alkaline glycerine phase. Because of the need for equimolecular amount of alkali to FFA content this technique can be applied to relatively low FFA level stocks, such as used and rancid cooking oil. It is clever, if the recycle into FFA and conversion into FAME (recuperation) is economically feasible. The prime operational problem is related to surface activity of the soap by measurable amount of useful components being dragged into the waste stream. Washing and drying operations are sources of loss in neutralization techniques. Practical consequences are loss of yield and environmental burden to wastewater treatment. To recuperate valuable feedstock components for biodiesel, the reverse of reaction 1 is to be applied to water phase. It is done by acidulation; FFA is separated into the extracted supernatant layer. For improving efficiency an apolar solvent can be beneficial, such as hexane. There have not reports of this in practice.

Neutralization treatment techniques have not been proven to be efficient for beef tallow, pork lard and chicken fat for the sake of processing the neutralized stream to standard quality biodiesel in alkali catalyzed transesterification [12]. Typical losses associated to neutralization have been recorded in technologies with heterogeneous catalysis by blocked active sites of the catalyst [13].

1.2.2 Degumming

A plausible explanation why conversion of neutralized streams to methyl esters has been inadequate or failed completely was mostly due to colloid chemical interactions. Soluble impurities, of concern FFA, phospholipids, high molecular weight esters and waxes challenged common processing routines. Gums are categorized as hydratable and non-hydratable and FFAs are separated in reactive extraction (reaction and washing) processes, called degumming. Hydratable impurities are best separated by hot water extraction; non-hydratable impurities necessitate reactive extraction into water soluble products. References in patent and scientific literature mainly focus on refining to improve process efficiency by reduction of specific consumption and losses. Degumming is challenging because of specifics features of the colloid system. Acidic actions are needed to break these molecules. These often possess surface activity that results in even higher losses in extraction. Small amount (0.002 to 0.1%) of phosphoric acid or citric acid is mixed with the fat under high shear at high temperature (60-90 °C). To reduce specific consumption and rate of losses the use of "synergistic blend" of phosphoric acid and citric acid has been claimed [14]. Enzymatic treatments have been proposed as alternatives to acids [15]. In removal of non-hydratable gums, mainly phospholipids, are precipitated under specified shear rate mixing, and additional neutralization under moderate shear rates followed by washing (extraction) of the fatty layer with sufficient water in sufficient number of steps until the oil becomes neutral. This kind of treatment not only consumes high amounts of water but the more water is used, the higher the loss of fatty materials that are vulnerable to form emulsion. This can have definite downstream consequences in difficulties in treatment of waste-water effluents.

Colloid characteristics of refuse stocks have been considered [16] by the use of surface activity modifying agent, sodium salt of EDTA (Ethylene-Diamine-Tetra-Acetic Acid). Fat, surface active agent and reactive solvent are mixed under high shear conditions in complex, but controlled emulsification process. In breaking the emulsion separation of gum components showed improved selectivity due to low stability of the emulsion in splitting by centrifugation followed by ultrafiltration membrane treatment. Lower specific consumption of auxiliaries and energy is key benefits.

1.2.3 Dewaxing

Waxes are crystallizable high molecular weight esters that are outside the accepted components in standard biodiesel, in commercial terms these make part of category U. Monounsaturated waxes are formed by esterification of long-chain saturated fatty acids and mono-un-saturated alcohols. They have 32-45 carbon molecules in chain. Waxes should be separated both to meet cold temperature and carbon number requirements. Crystallization is referred as “winterization” in edible oil processing. To improve the operation crystal nucleation aids can be used, to initiate nucleation and crystal growth in oversaturated solid-liquid system around. Crystal growth does not necessitate having oversaturation. Nucleation is done under low shear rate and controlled cooling rate to 20-5 °C/min [16]. Crystal growth results in a structure of adsorbed layers that increases the size of solid particles. Large size crystals are separated by filtration. Deposition in this adsorbed layer is not limited to wax components, but oil and other ingredients can be captured within, depending on operational conditions influencing selectivity and efficiency. Without strict control of nucleation and crystal growth rough disperse agglomerates can incorporate liquid components in the disperse wax crystal network. Petroleum ether, nC_6, ethanol and acetone have been found to control selectivity and promote reduction of loss in wax fractionation [17, 18]. By the use of a scheme with a solvent wax separation and splitting is done at high rate of solvent to oil (10:1), cooling temperatures can be as low as -20 to -50 °C as in the Emersol process. Lessons learned in lubricating oil dewaxing can significantly improve separation and specific consumptions of materials and energy even in splitting saturated and non-saturated glycerides, fatty acids.

1.2.4 Bleaching

Bleaching is an adsorption operation. It removes polar constituents that adhere onto a captive surface of a porous adsorbent. Bleaching earth and macro porous ion exchange resins can be engaged.

1.2.5 Distillation under High Vacuum

Vacuum distillation is to remove odorous components of frying oils. As reported by Crvengros [19], it is possible to apply vacuum distillation in thin film column, but our experiments showed that even under 0.001 bar pressure the temperature of the liquid phase exceeds 200 °C, and the amount and consistency of residue were so high that we skipped this treatment as a possible route of refining.

1.3 Less Common Techniques

1.3.1 Glycerolysis

It has been in use to avoid formation of polar and apolar phases difficult to separate due to high surface activity of soaps. Soap can be beneficial to promote phase transfer, but detrimental by exerting resistance to separation of phases. In reactive neutralization by glycerolysis is associated with formation of water and surface active glycerides that can be trans-esterified to improve products yield:

$$aFFA + bG \Longleftrightarrow c_1MG + c_2DG + c_3TG + \left(\sum c_i H_2O\right)$$

❼

Jackam converted high FFA feedstocks to biodiesel and concluded that refuse stocks can be best processed by glycerolysis [20]. A feedstock containing 15% FFA was reacted with glycerol at 230 °C for 150 min; the FFA level was dropped to 1% The higher the FFA level the longer time in processing must be applied. With a feedstock contenting 50% FFA, reaction was conducted for 240 min at 230 °C presence of Zn catalyst. Water was removed as formed, final FFA content was still high for accepted conventional alkali transesterification limits (6.5%) [21]. Reaction conditions for glycerolysis by the use of solid catalyst have been conducted at 240 °C and 20 bar [22].

Zn-Al_2O_3, TiO_2 and strongly acidic ion exchange resins have been claimed to be efficient solid catalysts for glycerolysis.

1.3.2 Preferred: direct esterification

Direct esterification—value chain optimization—is the most common treatment step in 2nd generation FAME process technologies. A pioneer and market leader is BDI-BioEnergy International GmbH. We have seen improvement potential in terms of efficiency, feasibility and ecology attributes by operating at lower excess of reagent, use of less catalysts than those reported as specific consumptions in laboratory and industrial practice [23]. We have limited ourselves to state of the art industrial techniques of 2nd generation technologies without the use of kinetic barriers removal by the use of high specific energy consuming technique such as microwave or supercritical conditions. Microwave assisted technique showed slow kinetic progress, even with model compounds [24]. On the other hand, supercritical conditions require high energy input, 100 bar pressure and 280 °C temperature [25] and even more severe conditions. Our aim was to use proprietary solvent borne technique to remove barriers of phase transfer to bring reaction partners into intimate contact without the need for severe operational conditions. The role of solvent is to wave interfacial resistance between substrate, reagent and catalyst and bring them into a single phase and to shift the reversible reaction toward the desired direction by removing the byproduct that would take place in the backward reaction, and by sweeping active site blocking components from the catalyst. A list of potential catalysts for this purpose is presented in U.S. Pat. 4,698,186 [26]. Second generation biodiesel technologies practice this by conversion of FFA with sulfuric acid catalyst, 12-60 times excess methanol to stoichiometry and hours in processing. The higher the FFA level, the higher the amount of catalyst recommended. Canacki [27] concluded that for a 50% FFA feedstock it is necessary to use at least 5% catalysts, relative to the amount of oil and an excess of 200 times to stochiometry for efficient esterification. We have considered it excessive and looked for better efficiency conducts.

By the use of truly continuous process technology of QS Biodiesel we successfully tested to convert 12.5% FFA containing corn oil Distiller's Dried Grains with Solubles (DDGS) into biodiesel at pilot scale. The product biodiesel did fully meet specifications for automotive fuels at much lower footprint and better specific consumptions and efficiency than state of the art techniques do. Losses have been comparable to MIU level of the feedstock. Lessons learned from this work constituted corner stones to dealing with refuse fat.

2. Methods and Data

2.1 Feedstock

Fats of category 1/2 of ATEV processing system were used in treatment to convert this byproduct of processing into a product that can be brought to market for biodiesel processing. Standard test methods have been employed as listed in Table 1. Fat samples have been solid and brown in color. It was free of plastics. Esthetic and (mal)odorous aspects of the feedstock have been observed in experiments to protect personnel. Before operation the fat was heated to 60 °C and homogenized by mixing. Experiments have been performed with homogenized sample. Two samples have been collected, Sample A was used for the baseline and Sample B for reliability checks. Gas chromatographic fatty acid compositions are given in Table 2. There have not been applied pretreatments, like preliminary settling, filtration or dehydration by any means.

2.2 Storage Stability Tests

Storage stability tests have been carried by keeping 10 g of fat in test tubes in oven at 40 and 60 °C for a period of 40 days. There have been 5 conditions in the accelerated storage stability test: (1) open test tube; (2) closed test tube; (3) in open test tube with addition of 10% water; (4) in closed test tube under inert gas blanketing; (5) in closed vessel under vacuum. FFA and insolubles in nC_6 have been tested in periods of 5 days.

2.3 Solvent Extraction

Temperature controlled, jacketed mix and settler equipment was used to test possible use of polar solvents for efficiency in removing impurities of category 1/2 fats, as practiced in petroleum refinery technologies to remove polar impurities. The temperature controlled jacketed unit was 500 mL in volume and an overhead stirrer mixed the solvent(s) and the fat, the stirrer was conducted through an overhead reflux cooler. Weighed amounts of solvents and fat samples have been mixed and heated to selected temperature. Times of operation: mixing 30 min, settling 30 min. Solvents from both phases have been recycled by distillation.

2.4 Bleaching

Bleaching was performed by mixing 50 g fats with bleaching earth. Bleaching earth was dried at 105 °C in vacuum oven and kept in dessicator prior use. Mixing was done by the use of an overhead stirrer at 110 °C for 30 min. The mixture was brought to filtration by the use of 0.45 micron filter, moderate vacuum was applied to control filtration rate.

2.5 Glycerolysis

Experiments have been performed under atmospheric and moderate pressure conditions. A 3 neck, 250 mL flask, equipped with extractive distillation condenser was used under atmospheric conditions. To further control and push the reversible reaction toward esterification we placed molecular sieve of 3A into the upstream section of the condenser to adsorb water. As there have not been measurable differences in separation and monitoring the progress in amount of water separated by extractive distillation we have discontinued using this technique. Reaction temperature was controlled by selecting the solvent by boiling point features, hexane was the lowest boiling point and hydrogenated, low in aromatic hydrocarbon mixtures for higher reaction temperatures.

Higher temperature experiments have been carried out in a 500 mL stainless steel bomb reactor. Pressure was controlled to keep the solvent mostly in liquid phase. Pressure was applied by repeated filling and rinsing the reactor with inert Nitrogen blanketing. Pressure range was set to 10-20 bars for temperature range of 110-220 °C. Under such conditions all solvents were condensable. On completion the processing time, the reactor was cooled by immersion into cold water. Prior to dismantling the excess nitrogen gas was released to the atmosphere through an intermediate impinger, filled with water. Catalysts tested were ZnO, H_sSO_4, and highly acidic ion exchange resins. We have been highly limited in using ion exchange resins because upper temperature for commercial resins can not go above 160 °C. This has been encumbered by blocking deactivation of deposits caused by MIU components.

2.6 Direct Esterification

Batch experiments were performed as described for deacidifying by glycerolysis under atmospheric and higher pressure conditions in the same apparatus, and same routines. The key difference was use of methanol (MeOH) as reagent instead of glycerol and inclusion of cationic exchange resin—GF101—as catalyst. Lewatit® GF 101 has been particularly recommended by LanXess for reduction of FFAs in triglycerides prior transesterification to biodiesel. The solvent used was solely hexane, nC_6.

Counter current atmospheric esterification has been performed under in glass equipment in a system illustrated in Fig. 2. Column height: 2.1 m, column diameter: 40 mm, packing: Rashig rings of 5 mm. Preheated fat and solvent mixture were fed into the column by a metering pump at a height of 20 cm from the bottom, preheated reagent and catalyst mixture were administered at a height of 20 cm from the top of the column. Both entry points have been protected by check valves. Interface layer was controlled at the bottom of the column, at a height of 5 cm from the bottom; solenoid valve was operated on conductivity basis. Evaporation of solvent and reagent was controlled by the use of overhead condenser. The pH of the product and temperature of the column, at 3 points have been checked.

2.7 Vacuum Distillation

Experiments were conducted under 0.01 bar pressure in 500 mL flask, heated by electric mantel. Final bottom temperature reached 360 °C. 30 cm high, vacuum jacketed 30 mm dia., column was filled with Rashig rings of 5 mm. No reflux was employed.

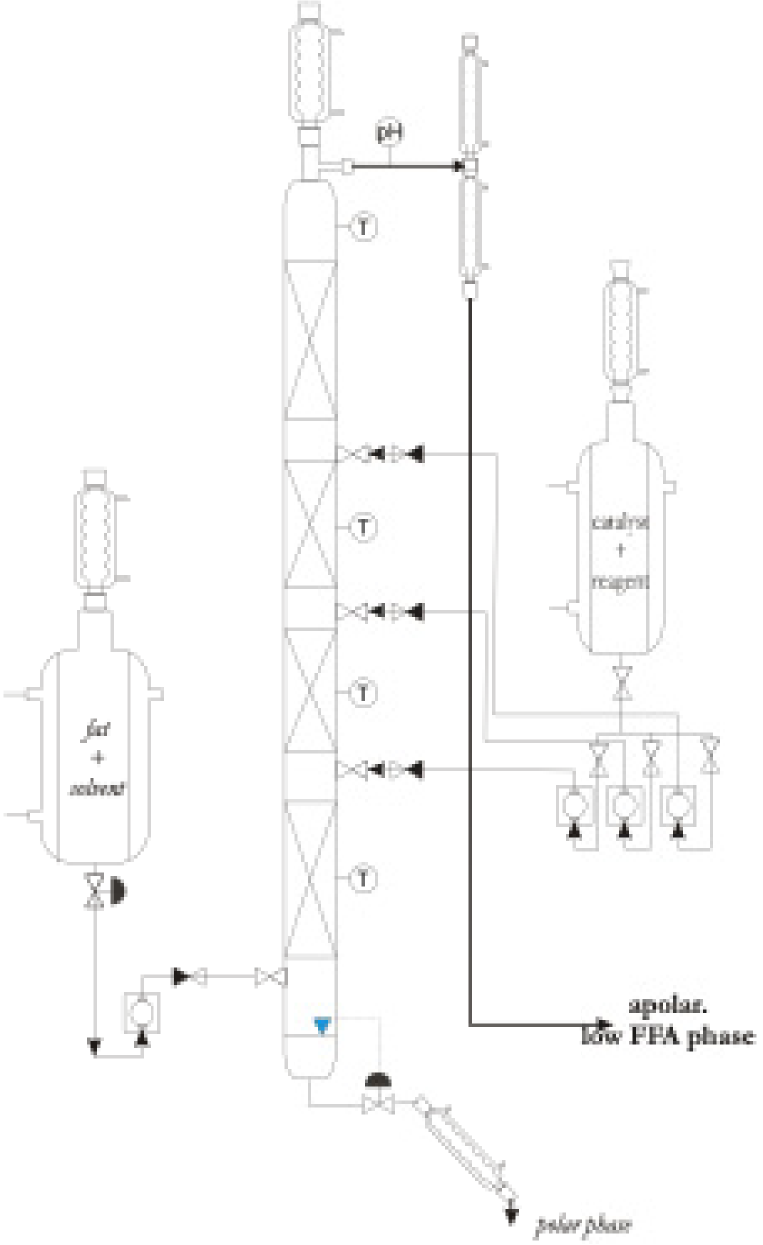


Fig. 2 Counter current laboratory esterification set-up. Re + C: methanol + catalyst; R: raffinate, esterified stream; S + F: refuse stock dissolved in hexane; G: glycerol phase; jackets are heated/cooled according to needs, dimensions are given in mm.

3. Results

Both refuse fat samples analyzed were very high in FFAs and exceeded those basic MIU characteristics that would make possible to process in first generation technologies. High FFA and MIU values set special consequences to feedstock treatment and challenged to achieve target yield value of 95%. It has been further complicated by high level of non-saponifiable constituents contents. This warns of difficulty to achieve a target ester content of at least 96.5% as requested in relevant biodiesel product standards. From chain length perspectives the feedstock makes possible to synthesize standard fatty acid (methyl) esters within the range of C_{14}-C_{24} chain length.

3.1 Storage Stability

Changes in FFA levels are given in Fig. 3. Data of insolubles in nC_6 are given in Table 3. These data show that these stocks have already been degraded in hauling and storage to a given level, further changes have not been significant in terms of acidity. Unexpected decrease in acidity in accelerated heat treatment is in accordance with combined action of degradation and deposits formation. The more degradation products formed in radical chain reaction mechanism the higher the deposition rate in the multi-phase system. Presence of water promotes separation of oxidized products into the deposit, as indicated by the amounts of insolubles in nC_6. Those advanced oxidation products that have sank into the deposit bypass neutralization in the test procedure. Even though, deteriorations have been within narrow range, that compares to uncertainty of the test.

3.2 Solvent Refining

Common problems observed have been low selectivity and high losses to the extract phase. These have been common for THF (Tetra-Hydro-Furan), DMSO (Di-Methyl-Sulfoxide), NMP (N-Methyl-2-Pirrolidone) selective polar solvents alike. High solvency of THF made not possible separation of phases. Separation could not have been improved significantly by employing duo-sol technique by addition of an apolar diluant solvent, to an extent of 50%. The use of water or glycerol as anti-solvent in an amount of 1-5% could neither improve separation, nor control solvency and selectivity. Polar solvents showed preference to preferentially extract lower molecular weight FFA. NMP seemed to be the most beneficial, probably because of its slight alkali character, but these exercises have not supported a decision to further explore it. The idea, inherited from petroleum refinery practice, to refine category 1/2 fats by the use of a selective polar solvent has been discarded.

3.3 Bleaching

Results of bleaching are given in Table 4. As expected this treatment removed most of the mechanical impurities, expressed in terms of nC_6 insolubles, and water, but on the expense of losses in yield, without having any measurable reduction in FFA level. Losses in yield were reduced by the use of apolar solvent, which acted to reduce viscosity and influenced colloid chemical features. But the expense of solvent separation was not beneficial to overall economy of operation. Reduction of MIU was not associated with reduction in extent of non-saponifiable components. It is to conclude that bleaching can have positive impact on esthetic of the sample, but not on processability. This conclusion is valid to those bleaching earth adsorbents that are used in edible oil processing. Non-saponifiables remained at similar level as in feedstock, at about 2%.

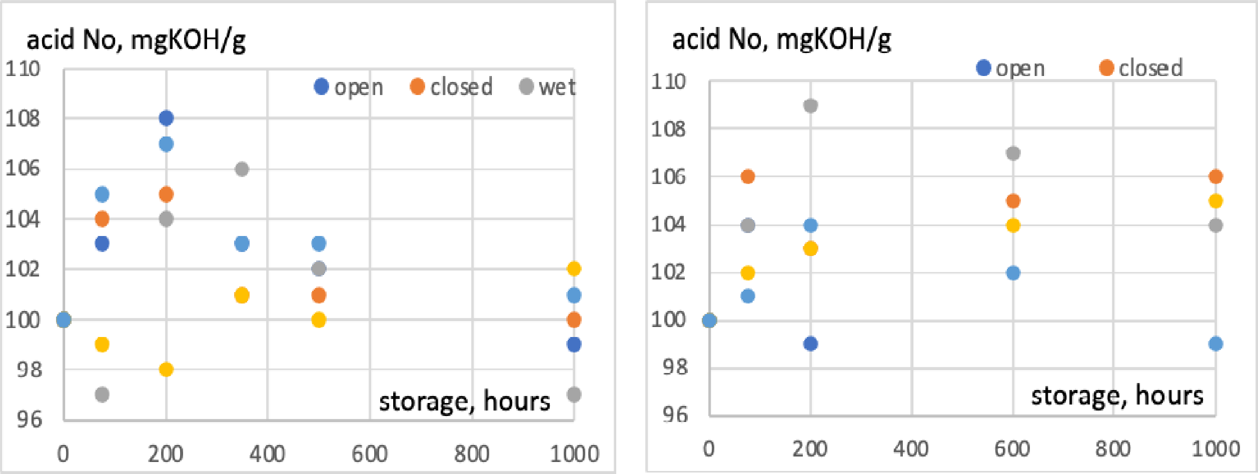
3.4 Glycerolysis

Most beneficial conditions and perspective to use at industrial case have been the followings: temperature: 180 °C; at a rate of 0.85% referred to fat feedstock, solvent nC_6, rate: fat: nC_6 = 1:1.15 (g:g); reagent rate: glycerol: fat = 1:3,6 (g:g); results of the most beneficial conditions are given in Table 5.

Table 1 Feedstock characteristics.

Characteristics	Unit	Method	Target value	Sample A	Sample B
Free fatty acid	mg KOH/g	ISO 6619:1988 ASTM D 664	10	100	107.6
Free fatty acid	%	ISO 6619:1988 ASTM D 664	5	50	54.8
Saponification No.	mg KOH/g	ASTM D 94	n.a.•	172	173
Water content	%	ASTM E 203-96	0.5	2.76	1.25
Impurities	%	EN12262	0.15	0.47	0.88
Unsaponifiable	%	AOCS Tk. 1a-64	0.85	1.50	2.07
Sulfur content	mg/kg	EN ISO 12937	50	150	320
Viscosity	mm^2/s	ISO 3960	n.a.	49.3	45.6
Pour point	°C	Own	n.a.	34.5	35.7
MIU	%	Calculated	1.5	4.73	4.2
GC test	%	EN 14103:2003	C_{14}-C_{24}	Passes	Passes

• Note: n.a: not applicable.



(a) Storage @ 40 °C

(b) Storage @ 60 °C

Fig. 3 Storage stability—acid number results.

Table 2 Fatty acid composition by gas chromatography.

Component		C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20+
Sample A	%	0.1	2.47	27.98	16.87	40.62	8.94	0.51	2.51
Sample B	%	0.06	2.35	26.37	18.13	42.17	9.01	0.47	1.44

Table 3 Deposits formation in storage stability tests.

Mode of storage	No.	Open	Closed	Wet	Vacuum	Blanketed
Insolubles @ 40 °C, mg/kg	0.45	2.37	1.21	2.87	1.11	1.17
Insolubles @ 60 °C, mg/kg	0.45	3.46	2.89	2.97	2.99	2.37

From the viewpoint of catalyst selection H_2SO_4 proved to be the best selection. It was weaker in deacidification, if compared to ZnO solid catalyst, but controlled lower rates to condensation of glycerides. Ion exchange resins have been weaker in efficiency than H_2SO_4 but produced lower yields, most evidently because of colloid chemical difficulties, which appeared in the form of an intermediary heterogeneous phase between the product apolar phase and the byproduct polar phase. The use of nC_6 solvent made possible to use technical grade glycerol in selected experiments.

Table 4 Bleaching—adsorption refining—test result.

Bleaching earth, %	0.5	1	2
FFA, mg KOH/g	100.2	100.0	100.1
Amount on filter, g/50 g	1.12	1.73	3.74
loss, %	2.2	3.4	7.5
Loss: bleaching earth rate	2.24	1.73	1.87
Sulfur content, ppm	152	155	151
Appearance			

Table 5 Results of the most beneficial pretreatment means.

Characteristics	Unit	Glycerolysis	Direct esterification	
			Batch	Counter current
FFA	mg KOH/g	2.57	2.80	10.0
Reduction	%	97.4	97.2	90.0
Yield	%	91.7	92.3	94.4
Saponification No.	mg KOH/g	177.6	182.4	176
Moisture, M	%	0.003	0.001	0.001
Impurities, I	%	0.09	0.001	0.001
Not saponifiable, U	%	1.51	1.53	1.50
Sulfur content	mg/kg	92	88	52
Viscosity	mm^2/s	64.8	5.82	14.3
MIU	%	1.60	1.53	1.50
Pour point	°C	35.0	-1	5

It has been common to glycerolysis exercises that FFA levels have been significantly reduced to an extent of 50 to 97.5%, moisture and impurities levels have been almost completely removed, but the amount of matters not saponifiable has not been affected. A slight decrease in sulfur content has also been observed. Yields above 90% show potentials in glycerolysis pretreatment, but having in view higher yield figures in esterification we would not insist on employing this treatment.

Major drawbacks and counter arguments to use of glycerolysis as a pretreatment technique, consisted of raised viscosity and no change in amounts of not saponifiables. This raise in viscosity indicates formation of poly-glyceride condensed structures. This is a challenge to achieving the required ester content in biodiesel requested by standards (96.5%). Downstream biodiesel synthesis experiments showed that these condensed structures do break into FAME if optimal reaction conditions are applied.

3.5 Direct Esterification

Direct esterification resulted in more beneficial results than glycerolysis. Results in the truly counter current mode of operation are given in Table 5. Conditions of counter current test: pressure: atmospheric, solvent (n-hexane) to feed (Sample B) 1:3 (vol:vol); feed rate: S + F in: 150 mL/h (fat: 37.5 mL/h); reagent MeOH + H_2SO_4: 120 mL/h, mean temperature: 52 °C, pH of raffinate stream: pH = 1.3.

It should be stressed that counter current experiments have been done in a short column, under atmospheric pressure just to demonstrate that it is possible to treat difficult refuse stocks to achieve the expected quality by the use of counter current technique with the condition of employing higher pressure and higher temperature.

3.6 Vacuum distillation

Vacuum distillation has not been worth considering as a viable operation because of foam formation and deposits formation in the bottom product due to thermal instability. FFAs were separated as distillation products to an almost complete recuperation, even though we have discarded this option to be considered in a retrofit activity of small and medium size units.

4. Conclusions

Refuse stocks are vulnerable to handling and storage conditions. Losses in property should be avoided by employing protocols to shorten storage periods, controlling degradation promoting conditions, such as contact to air and water and passivating catalytic surfaces of storage tanks.

Technologies employed in edible oil and grease processing practice do not meet expectations—feasibility criteria—in terms of efficiency and yield.

Glycerolysis and direct esterification are both efficient techniques to reduce FFAs content and levels of impurities if proper operational conditions are employed. The use of apolar solvent has been beneficial for both treatment techniques to improve refining efficiency, to promote conversion and to shift equilibrium of the reversible esterification reactions toward the desired direction. The use of an apolar solvent contributed to almost complete dehydration and impurities separation of the stocks possible.

In glycerolysis reactions H_2SO_4 catalyst outweighed ZnO in milder in controlling polycondensation of glycerides for the sake of more proficient downstream processing into biodiesel.

Direct esterification has been concluded to be the most beneficial pretreatment from biodiesel processing technology perspectives for small and medium scale units. It is recommended to consider in retrofitting 1st generation units to systems that can process inferior quality, but inexpensive refuse stocks.

The use of the solvent born techniques made to release interfacial tension, to promote intimate contact of reaction products and to sweep and separate reaction products from active sites into different phases and makes it possible to execute operations in truly continuous mode of operation, even under atmospheric conditions.

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