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Investigation of Waste Cooking Oil processing using HAAS automated reactors system

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The processing of waste cooking oils (WCO) is a complex process that heavily depends on their chemical and physical properties. The work described in this article includes research on the processing of WCO samples using transesterification methods. An automated reactor system Matrix9 HAAS was used to perform process studies and FT-IR measurements.

Transesterification of oils in the presence of KOH might be directly applied as the optimal one for oils with a low acid number, while for oils with a higher acid number an additional esterification step is advisable in the presence of an acid catalyst or under conditions of high temperature and pressure.

Keywords: waste cooking oil (WCO), transesterification, Matrix9 HAAS reactors system, processing contaminated oils, chemical reactors.

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INTRODUCTION

Increasing public and institutional awareness of the need to protect the environment over the past decades has contributed to increased insistence and the need to improve existing technological processes in this regard. Commercially run processes should have as little impact on the environment as possible and comply with the concept of a closed-loop (recirculating) economy. An example of the development of treatment processes can be the use of new, increasingly sophisticated reaction systems, including multi-reactor systems[1–3]. The reaction systems may operate in parallel or in series, and give the possibility of precise control and setting of processing parameters. This gives the possibility of flexible operation with different raw materials. This also applies to the processing of waste cooking oils (WCO).

The processing of waste cooking oils makes it possible to manage a large group of wastes that were previously disposed of by combustion. Waste oils may be used, for example, to produce biofuels or plastics[4–6]. The production of biofuels is a particularly interesting area for processing research because of the high demand for renewable and controllable energy sources, as well as the possibility of using a wide range of different waste oils and waste fats with different chemical structures.

Demand for oil is expected to exceed its current production by no more than 50 years[7], creating the drive to find oil substitutes such as biofuels, and is an important part of many countries' development plans. The European Union has introduced Directive "2008/0016 (COD)" aimed at increasing the use of energy from renewable sources, including increasing the share of biofuels in conventional fuels. In turn, diesel fuel with a 5:1 ratio of soybean oil has come into use in the US market[8]. The advantage of using biofuels is the low content of sulfur compounds (impurities present in the fat used to obtain biofuel, especially in waste fats), which have a corrosive effect on installations designed for fuel combustion and contribute to the formation of sulfur oxides that pollute the atmosphere[9]. There is also the advantage of easily obtainable raw material for production and a solution in the area of the problem of oil disposal.

Waste edible vegetable oils, including soybean oil, palm oil, rapeseed oil, sunflower oil, non-edible vegetable oils, such as bitter almond oil[10, 11], and animal fats, such as waste fat from slaughtering poultry, may be used to produce renewable fuels[12]. Due to the different fatty acid profile characteristics of the feedstock, the composition of the esters in the resulting biofuel will also be different. Globally, it is estimated that approximately 20–32% of all waste oils are waste edible oils[13]. Due to the different fatty acid profile characteristic of the feedstock, the composition of the esters in the resulting biofuel will also be different. In the USA, the amount of waste edible oils reaches 100 million gallons per day, where the average per capita consumption is about 4 kg per day. In Canada, similar to the US, approximately 4 kg of WCO per day per person is produced, which, with a population of 33 million, translates into nearly 10 million tonnes of waste per year. In the European Union, the amount of waste of edible oils varies between 700 000 and 1 million tonnes per year. In the UK, more than 200,000 tonnes of WCO are produced annually[13], and in China around 5 million tonnes per year[8, 14]. The oil may require preprocessing prior to processing, which may include dissolution of solid fats, filtration of impurities, removal of water, degumming, among others. A further step is the transesterification of the triglycerides comprising the oils into fatty acid esters, either in the presence of a base catalyst, an acid catalyst, or by an enzyme-catalysed process[8, 15]. Due to the short reaction time and low price of the substrates, the first two transesterification methods are used on an industrial scale for selected substrates[16, 17], but attempts are also being made to apply enzymatic transesterification industrially[18, 19].

Processing of waste oils by transesterification on an industrial scale faces problems that are related to the variety of input feedstocks. The waste oils may vary significantly in their free fatty acid (FFA) content and thus acid number. Without adapting the process to the raw material being processed, it is possible to cause a significant reduction in the efficiency of the transesterification process. A high FFA content leads to increased soap formation, which makes separation of the biofuel difficult or even impossible. They may also negatively affect the kinetics of the transesterification process, partially reversing it back to the substrates[20, 21]. Only oils with an FFA content of less than 0.5% are suitable for direct transesterification reactions[22]. WCOs contain more than 10% FFA, which requires different reaction conditions or a prior esterification reaction of FFA to esters in an acidic medium[23]. The pursuit of industrial application of enzymatic transesterification is related, among other things, to the high resistance of this process to the high content of FFAs, which may also be converted to esters without additional steps[24]. Alternatively, catalyst-free transesterification may also be conducted under supercritical conditions, with increased temperature and pressure, with the addition of methanol or ethanol[25]. This reaction would be difficult to apply on an industrial scale due to the demanding process conditions. The esters may be a feedstock for biofuel production. Biofuels obtained by transesterification may require additional post-treatment, such as the introduction of additives or the removal of water by distillation. Here, distillation will have the task of bringing the fuel up to current quality standards[26, 27].

The zero-emission green fuel obtained from WCO may be used in conventional compression-ignition cars without prior modification. By-product fatty acid salts (i.e. soaps) formed during the process are used as surfactants, characterised by high biocompatibility and biodegradability[28]. Alternative applications of esters containing long-chain fatty acids are the production of food emulsifiers, characterised by higher stability and small dispersed particle size[29], the production of lubricants[30], cement additives[31], or other reagents[32].

The subject of the work presented below was to study the transesterification process using selected rapeseed oils with different degrees of processing as an example, and to determine the optimum transesterification procedures for oils with specific acid number ranges, using the multi-reactor system Matrix 9 HAAS.

MATERIALS AND METHODS

Reagents

Waste cooking fats (after heat treatment) – rapeseed oil samples (Table 1) – obtained from industrial sources (restaurants) and households were used to conduct the transesterification reaction.

The oils obtained were analysed to determine the acid number using the titration method according to the procedure in PN-EN ISO 660:2010 (approx. 0.1 N KOH solution in EtOH). Oil G (Ollineo, Netto Sp. z o.o.), which is fresh rapeseed oil not previously heat-treated, was used in the syntheses for comparison with waste oils. Methanol (AR, Chempur), potassium hydroxide (AR, Chempur), acid cationite (Dowex 50W-X8, Sigma-Aldrich), 98% concentrated sulphuric acid (AR, Chempur) and anhydrous magnesium sulphate (VI) (AR, Chempur) were also used in the syntheses.

Table 1. Waste rapeseed oil samples

Name of oil sample	Description	Acid value (mg KOH/g)
A	Oil obtained from industrial sources	2,3
B	Oil obtained from households	0,9
C	Oil obtained from households	0,4
D	Oil obtained from households	0,5
E	Oil obtained from industrial sources	1,5
F	Oil obtained from households	2,5
G	Fresh (untreated) oil	0,3

Transesterification methods

1. Direct transesterification with KOH and MeOH.

A sample of oil, MeOH and KOH (exact amounts given in Table 2) were introduced into a pressure stainless steel reactor and the reactor was sealed. The reactor was flushed with argon (flushing lasted 10 minutes, with a flow rate of 50 ml/min) to prevent uncontrolled oxidation of the oil in an air atmosphere. The reactor contents were then stirred (250 RPM) and heated at 60 °C for 2 h. Once the process was complete and the reactor cooled down, the mixture was transferred to a separator. Using the separator, the glycerol phase containing KOH and the residual MeOH was separated from the organic phase. The organic phase was then washed 3 times with brine solution, each time the upper phase was collected. The organic phase was dried with anhydrous $MgSO_4$, which was separated by vacuum filtration. The product – biofuel – was obtained and its volume was measured.

A simplified process flow is shown in Figure 1.

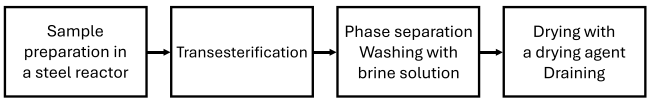


Figure 1. Schematic of the sequence of steps of operations in method no. 1

2. Transesterification with KOH and MeOH, preceded by esterification in the presence of H_2SO_4.

An oil sample, MeOH and H_2SO_4 were introduced into a reactor made of borosilicate glass. The glass reactor was used in the process due to the corrosive environment - the use of concentrated H_2SO_4. The mixture was stirred (250 RPM) and heated at 65 °C under a reflux condenser for 2 h. After the process, the mixture was cooled and transferred to a separator, with which the glycerol phase containing H_2SO_4 and the MeOH residue were separated from the organic phase. The mixture was then washed 3 times with brine solution, each time the upper phase was collected. The organic phase was dried with anhydrous $MgSO_4$. Anhydrous $MgSO_4$ was separated from the mixture by vacuum filtration. The esterified mixture was transferred to a pressure stainless steel reactor, where the actual transesterification process was carried out. MeOH and KOH were added to the mixture in the reactor, after which the reactor was sealed and flushed with argon (flushing lasted 10 minutes, with

a flow rate of 50 ml/min) to prevent uncontrolled oxidation of the oil in an air atmosphere. The mixture was stirred (250 RPM) and heated at 60 °C for 2 h. Once the process was complete and the reactor cooled down, the mixture was transferred to a separator. Using the separator, the glycerol phase containing KOH and the residual MeOH, was separated from the organic phase. The organic phase was then washed 3 times with brine solution, each time the upper phase was collected. The organic phase was dried with anhydrous $MgSO_4$, which was separated by vacuum filtration. The product – biofuel – was obtained and its volume was measured.

A simplified process flow is shown in Figure 2.

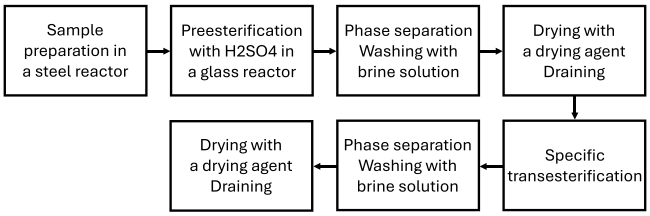


Figure 2. Schematic of the sequence of steps of operations in method no. 2

3. Transesterification with KOH and MeOH, preceded by esterification at 250 °C and 40 bar without the addition of an acid catalyst.

An oil sample, MeOH, was introduced into a stainless steel pressure reactor, after which the reactor was sealed and flushed with argon (10 min, 50 mL/min) to prevent uncontrolled oxidation of the oil in an air atmosphere. The reactor contents were then stirred (250 RPM) and heated at 120 °C or 250 °C and 40 bar pressure for 2 h. After heating was completed, the reactor was unsealed and KOH was added. After the reactor was sealed, the above procedure was repeated once more, but this time by heating the mixture at 60 °C. Once the process was complete and the reactor had cooled down, the mixture was transferred to a separator. Using the separator, the glycerol phase, containing KOH and the residual MeOH, was separated from the organic phase. The organic phase was then washed 3 times with brine solution, each time the upper phase was collected. The organic phase was dried with anhydrous MgSO4, which was separated by vacuum filtration. The product – biofuel – was obtained and its volume measured.

A simplified process flow is shown in Figure 3.

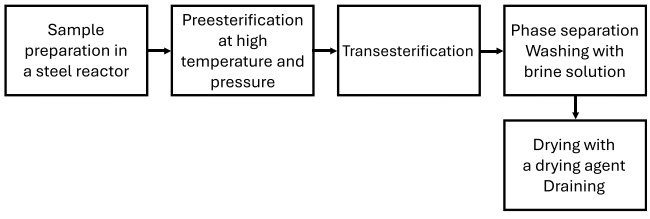


Figure 3. Schematic of the sequence of steps of the operation in method no. 3

4. Transesterification with KOH and MeOH, preceded by esterification in the presence of cationite.

A sample of oil, MeOH and cationite was introduced into a pressure stainless steel reactor, after which the reactor was sealed and flushed with argon (10 min, 50 mL/min) to prevent uncontrolled oxidation of the oil in an air atmosphere. The reactor contents were then stirred (250 RPM) and heated at 60 °C for 2 h. Once the process was complete and the reactor cooled, the resulting mixture was separated from the cationite and recirculated into the reactor, followed by the addition of MeOH and KOH. To conduct the transesterification, the mixture in the closed reactor was again washed with argon, stirred (250 RPM) and heated at 60 °C for 2 h. After completion of the process and cooling of the reactor, the mixture was transferred to a separatory funnel, Using the separatory funnel, the glycerol phase containing KOH and the residual MeOH, was separated from the organic phase. The organic phase was then washed 3 times with brine solution, each time the upper phase was collected. The organic phase was dried with anhydrous $MgSO_4$, which was separated by vacuum filtration. The product – biofuel–was obtained and its volume was measured.

Fresh portions of cationite were used in the reactions. It is also possible to regenerate the cationite by washing it successively with: acetone (to remove oil residues), methanol (to remove glycerine residues), 6 M HCl, distilled water, and finally again with methanol.

A simplified process flow is shown in Figure 4.

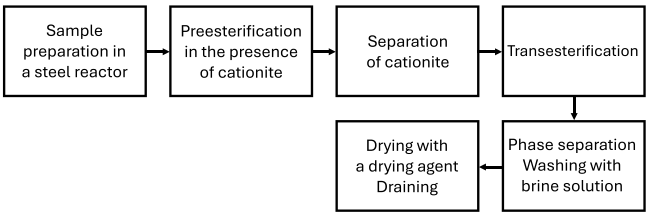


Figure 4. Diagram of the sequence of steps of operations in method no. 4

Each diagram (Figure 1–4) shows the sequence of steps in the processing of oils on an industrial scale for each of the four methods described above. High-temperature distillation under vacuum is conducted as the final step under industrial conditions. In the laboratory scale and in the processes conducted, distillation was not a key step for testing and evaluation of the results.

Table 2 shows the process parameters for the scheduled transesterification reactions of the oil samples.

Apparatus and measurements

FT-IR measurements

FT-IR measurements were carried out using a Thermo Scientific Nicolet iS50 FT-IR spectrometer, using liquid nitrogen to cool the MCT detector. The spectrometer was equipped with a Harrick Scientific Products FiberMate2 diamond-ATR optical probe.

Carbon content and heat of combustion measurements

Prior to the actual measurements, the Eltra CHS 580 analyser was calibrated using a 'premium coal' standard (Eltra 92550-3020). Each biodiesel sample container was shaken before the analytical sample was taken. A drop of oil was then transferred to a ceramic cuvette using a pipette. The weight of the sample was determined using an analytical balance (Radwag AS 220.3Y). The cuvette was then placed in the analyser, where the sample was combusted under a pure oxygen atmosphere and a temperature of 1350 °C. Analytical results consisted of mass fractions of carbon (C) and hydrogen (H). For the calorimetry measurements, the analytical sample was transferred to a stainless steel cuvette and the sample mass

Table 2. Schedule – summary of substrates and process parameters planned for transesterification

Reaction No.	Name of oil sample	Acid value (mg KOH/g)	Amount of oil sample (ml)	Amount of methanol (ml)	Stage 1			Stage 2			
					Catalyst type	Reaction temperature (°C)	Reaction time (h)	Additional amount of methanol (ml)	Amount of KOH (g)	Reaction temperature (°C)	Reaction time (h)
1	Sample A	2,3	633	140					13 g	60 °C	2 h
2	Sample A	2,3	633	140	2 g H2SO4	reflux	2 h	140	5 g	120 °C	2 h
3	Sample B	0,9	500	100	no catalyst	250 °C	2 h		5 g	60 °C	2 h
4	Sample C	0,4	500	100	2 g H2SO4	reflux	2 h	100	5 g	60 °C	2 h
5	Sample E	1,5	500	100					5 g	60 °C	2 h
6	Sample E	1,5	500	100	no catalyst	250 °C	2 h		5 g	60 °C	2 h
7	Sample E	1,5	500	100	ionite	60 °C	2 h		5 g	60 °C	2 h
8	Sample D	0,5	500	100					5 g	60 °C	2 h
9	Sample D	0,5	500	100	ionite	60 °C	2 h		5 g	60 °C	2 h
10	Sample G	0,3	500	100					5 g	60 °C	2 h
11	Sample F	2,5	500	100	no catalyst	250 °C	2 h		5 g	60 °C	2 h
12	Sample F	2,5	350	80					5 g	60 °C	2 h
13	Sample B	0,9	500	100	ionite	60 °C	2 h		5 g	60 °C	2 h

was determined using an analytical balance (Radwag AS 220.3Y). The cuvette was then introduced into a calorimetric bomb (Parr 6400), where it was combusted in an atmosphere of pure oxygen. The analytical result obtained determined the heat of combustion (higher heating value, HHV). The lower heating value (LHV) was calculated by subtracting the heat of vapourisation of water proportional to the amount of hydrogen in the sample, which was obtained by hydrogen volume analysis. The first sample analysed (sample 10) was analysed in triplicate. Single samples were analysed for the other materials.

MATRIX 9 HAAS reactor system

An automated multi-reactor system MATRIX 9 HAAS, designed to operate in a vacuum, at atmospheric pressure and under increased pressure, was used to conduct the process. The designed reactor system served as a universal reactors unit providing adaptability for combining reactors in different configurations within the needs of applying different methods and different stages for different qualities of waste oils with different acid numbers and degrees of contamination.

The automated multi-reactor system MATRIX 9 HAAS was equipped with FT-IR and Raman measurement capabilities (analytical apparatus equipped with measurement probes inserted into the reactor) to achieve versatility of application for single-stage and multi-stage processes requiring analysis. For the study of waste cooking oil processing, tests were carried out using FT-IR spectroscopy. Preliminary tests showed that measurements by Raman spectrometry did not give conclusive results to evaluate samples before and after synthesis. The process apparatus and equipment are shown on Figure 5.

A selection of reactors from the automated multi-reactor system MATRIX 9 HAAS was used for transesterification in a simplified configuration (pretreatment, transesterification, phase separation, drying and filtration).

Reactor made of stainless steel SS316, volume – 5 l, max. pressure 100 bar, max. temperature 250 °C, stirring 0–2000 RPM, with filter screen was selected for oil pretreatment, i.e. filtration of impurities of approx. 1 mm in diameter (use of filter screen).

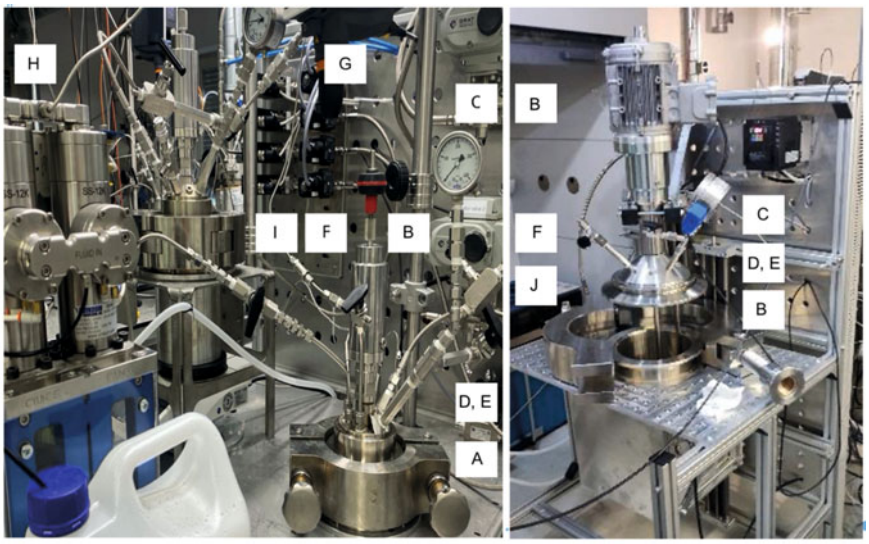


Figure 5. HAAS automated multi-reactor system MATRIX 9 used for modular adaptation of the number of reaction vessels and equipment to the needs of the transesterification reaction in progress. Components: A – 2 l reactor clamps and lid, B – mechanical stirrer drive, C – pressure gauge, D – safety valve, E – safety disc, F – gas purge line, G – mass gas flow controllers, H – metering pump, I – 500 ml reactor, J – 5 l reactor clamps and lid

Reactor made of stainless steel SS316, volume – 2 l, maximum pressure 100 bar, maximum temperature 250 °C, stirring 0–2000 RPM, was selected for pre-processing (excluding the H_2SO_4 method) of the oils prior to the actual transesterification (removal of free fatty acids).

Reactor made of borosilicate glass, volume – 2 l, non-pressurised, maximum temperature 200 °C, stirring 0–600 RPM, was selected for pre-processing of oils with H_2SO_4 prior to the actual transesterification (removal of free fatty acids).

Reactor made of stainless steel SS316, volume – 2 l, maximum pressure 100 bar, maximum temperature 250 °C, stirring 0–2000 RPM, was selected for the actual transesterification process.

Separation vessel made of borosilicate glass, volume – 2 l, non-pressurised, maximum temperature 200 °C, was selected for phase separation.

Reactor made of stainless steel SS316, volume – 0.5 l, maximum pressure – 100 bar, maximum temperature – 250 °C, stirring 0–2000 RPM, was selected for drying and straining the products obtained.

A borosilicate glass reactor was used interchangeably for syntheses conducted in the presence of H_2SO_4. Borosilicate glass reactor was selected instead of the 316 stainless steel reactor for the pre-processing due to the corrosive properties of H_2SO_4 under reaction conditions.

The Matrix 9 reactors set with the HAAS Matrix 9 software allows several reactions to be run in parallel or in series. It ensures that the oil with the higher acid number is pre-processed using the optimum method and that the intermediate is then added to the less thermally treated waste oil to economise the transesterification process. Another major advantage is the ability to scale up laboratory testing, i.e. working at a scale of 100 mL to 10 L with the possibility of increasing the maximum volume to 50 L for the pilot scale.

RESULTS

The first difficulty in preparing for the series of trials was to estimate the ratio of substrates, especially the initial ratio of MeOH to oil. Different values for the ratio of raw materials can be found in the literature. However, according to sources there should be an excess of MeOH relative to the oil, i.e. more than 3 mole of MeOH per 1 mole of oil. This allows the kinetics of the process to shift towards the formation of products (bioesters). Due to the diversity of oil compositions, the molar mass and density of individual samples may vary. In this paper, an average oil mass of 881 g/mol and a density of 0.91 g/mL were assumed for simplicity.

The minimum amount of methanol required for the exhaustive transesterification of 1 litre (~1.033 mol) of oil is ~125.36 mL (molar ratio of MeOH to oil 3:1). In most cases, ~500 mL of oil was used for the reaction. During testing, it was found that the molar excess of methanol could be reduced to a value of ~5.1 mol MeOH per 1 mol oil.

In the case of an alkaline catalyst, the use of a KOH amount of 0.8–2 wt% oil was reported in the literature[33, 34]. After a series of preliminary tests, it was found to be advantageous not to exceed an amount of about 1.6 wt% KOH per unit of oil, i.e. in practice about 5 g KOH per 500 mL of oil. The use of lower amounts of MeOH and KOH than those indicated in the literature led paradoxically to an increase in the amount of the final product obtained - fatty acid methyl esters. The amount of acid catalyst (concentrated H_2SO_4) and Dowex 50W-X8 cationite was assumed to be 2 g after literature analysis[33, 34]. Previous work reported an amount of about 1% cationite and about 3 wt% H_2SO_4, but such amounts for industrial conditions are significant, which would result in a significant amount of additional problematic effluent.

The reaction with the alkali catalyst proceeds most efficiently at about 60 °C. Trials at 120 °C were unsuccessful, manifesting the formation of a homogeneous solution. The indicated homogeneous solution could not be separated into a glycerol phase and an ester phase (Fig. 6A). A similar effect was also observed when using more than 5 g KOH per 500 mL of oil. It is likely that intermediate compounds acting as emulsifiers may be formed under these conditions. A possible reason for this is the partial re-esterification of glycerol into mono- or diesters, which are much more soluble in the excess monoester and the presence of excess methanol, at too high a temperature or with too much KOH. Such a homogeneous mixture transferred to a manifold and treated with brine forms stable, non-separable emulsions (Fig. 6B).

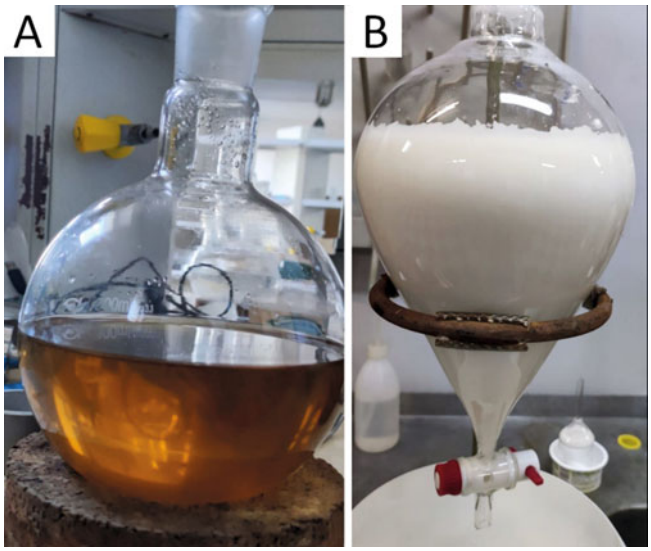
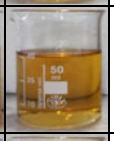


Figure 6. Solution after transesterification in which no phase separation has occurred (A); stable emulsion after the addition of brine to a solution in which no phase separation has occurred (B)

An expected post-transesterification reaction mixture should consist of two phases (Fig. 7). The upper phase is the bioester. The lower phase contains excess methanol, catalyst, saponified fatty acids and glycerol. The colour of the lower phase is usually darker than the upper phase, indicating that it takes with it the impurities present in the waste oil and those formed during the reaction. The post-reaction mixture tends to form emulsions, which requires time necessary for stratification. This also causes difficulties in 100% recovery of the organic phase on separation. In industrial settings, instead of the time-consuming separation by the above method, industrial centrifuges are used, which offer faster phase separation (no undesirable hydrolysis of the bioester and complete separation of the aqueous and organic phases). The results of the transesterification reactions performed are summarised and presented in Table 3.

Table 3. Results of transesterification reactions conducted using waste oil samples

Reac-tion No.	Name of oil sample	Acid value (mg KOH/g)	Sample amount (ml)	Product amount (ml)	Reaction yield (%)	Electricity consumption per process (kWh)	Appearance of sample oil as substrate	Appearance of sample bioester – product	Calorific value of crude oil (MJ/Kg)	Calorific value of bioester theoretical (MJ/Kg)	Molar ratio MeOH:oil*	KOH (wt%)***	Energy consumption per unit oil (kWh/kg)****	Energy consumption per unit of oil (MJ/kg)
1	Sample A	2,3	633mL	320 mL	55%	0,67			38	38,8	5,35:1	2,28	1,18	4,2
2	Sample A	2,3	633 mL	400 mL	69%	2,02			38	38,8	5,35:1**	0,88	3,55	12,78
3	Sample B	0,9	500 mL	350 mL	71%	5,32			38	38,8	4,83:1	1,11	11,82	42,55
4	Sample C	0,4	500mL	480 mL	98%	1,34			38	38,8	4,83:1**	1,11	2,98	10,72
5	Sample E	1,5	500 mL	475 mL	97%	0,67			38	38,8	4,83:1	1,11	1,49	5,36
6	Sample E	1,5	500 mL	450 mL	92%	5,32			38	38,8	4,83:1	1,11	11,82	42,55
7	Sample E	1,5	500 mL	420 mL	85%	1,34			38	38,8	4,83:1	1,11	2,98	10,72
8	Sample D	0,5	500 mL	470 mL	96%	0,67			38	38,8	4,83:1	1,11	1,49	5,36
9	Sample D	0,5	500 mL	460 mL	94%	1,34			38	38,8	4,83:1	1,11	2,98	10,72
10	Sample G	0,3	500 mL	455 mL	93%	0,67			38	38,8	4,83:1	1,11	1,49	5,36
11	Sample F	2,5	500 ml	320 mL	65%	5,32			38	38,8	4,83:1	1,11	11,82	42,55
12	Sample F	2,5	350 mL	300 mL	61%	0,67			38	38,8	4,83:1	1,59	2,13	7,66
13	Sample B	0,9	500 mL	480 mL	98%	1,34			38	38,8	4,83:1	1,11	2,98	10,72

*Average oil density of 0.9 g/mL and average molar mass of 880 g/mol were assumed for the calculations.
**All MeOH from step 1 has been removed.
***KOH wt% is given relative to the weight of the oil.
****The process was conducted in a laboratory scale reactor, which reduces the energy efficiency relative to the process in an industrial scale reactor.

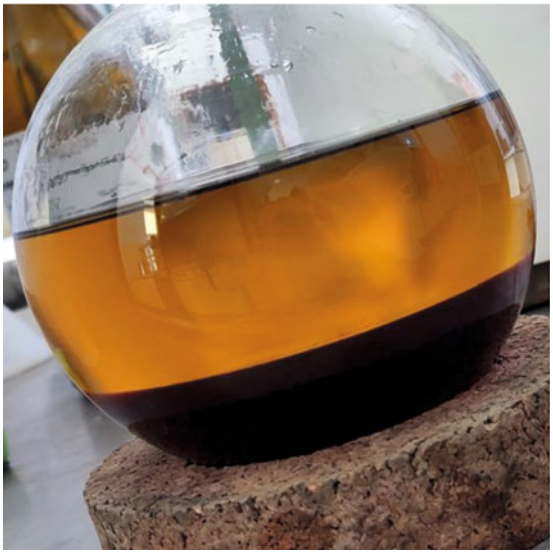


Figure 7. The transesterified solution that was separated into phases. The upper phase consists of the bioester and the lower phase consists of glycerol, methanol residues and oil-derived impurities

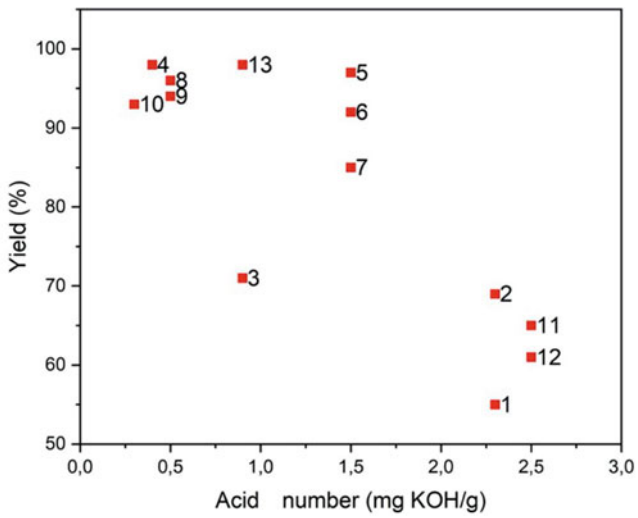


Figure 8. Correlation of acid number and transesterification reaction yield. The corresponding synthesis numbers are given next to each point on the graph

A correlation was observed between the yield and the difficulty of handling the reaction mixtures. Figure 8 shows the correlation of acid number on process yields for bioesters. For the syntheses for which oils with higher acid numbers were used, lower process yields were observed. This is mainly due to the presence of a higher amount of free fatty acids, which react with KOH to form more soaps. The higher amount of soap makes it more difficult to separate the glycerol phase from the ester phase, thus leading to the loss of some product during purification. For oils with an acid number of 0.3–1 [mg KOH/g], method no. 1 appears to be the most effective due to its energy efficiency, simplicity and ease of post-reaction treatment.

For oils with an acid number of 1–1.5 [mg KOH/g], the most effective method appears to be method no. 3, with pre-esterification at 250 °C and 40 bar (expensive in terms of energy due to the requirement to heat to 250 °C instead of 60 °C, and requiring a reactor with a pressure design of up to a minimum of 50 bar, which on an industrial scale creates an additional requirement for PED pressure certification), or method no. 4, i.e. a method with a catalyst in the form of cationite. For oils with an acid number between 1.5–2.5 [mg KOH/g], method no. 4 with cationite or method no. 2 with H_2SO_4 could be preferred. The method with cationite has the advantage that it does not need a separate glass or enamel reactor and requires a simpler methodology during the post-reaction treatment, as it is limited to draining the cationite and regenerating it before the next use.

Figure 9A shows the normalised FT-IR spectra of the biodiesel samples obtained after transesterification. In the range ~2800–3000 cm^{-1}, bands characteristic of stretching vibrations in C-H bonds in alkanes are visible. The band with a maximum at ~1740 cm^{-1} is associated with the presence of stretching vibrations of the ester C=O groups. The bands in the range ~1340–1480 cm^{-1} can be related to the bending vibrations of the C-H bonds present in alkenes. In contrast, the bands at ~1060–1260 cm^{-1} can be related to C-O stretching vibrations in esters. The band at ~720 cm^{-1} is associated with bending vibrations in C-H bonds. Figure 9B shows the FT-IR spectra of the starting oils used to synthesise the biodiesel samples and the spectrum of rapeseed oil without heat treatment. It can be seen that the degree of oil consumption has no significant effect on the profile of the measured spectra. The differences between the samples obtained and fresh rapeseed oil are shown in Figure 9C. The FT-IR spectra before and after transesterification do not differ significantly, which is related to the similar structure of the compounds. The main difference is the change in intensity of the band at ~1100 cm^{-1} (C-O oscillations), which has a much lower intensity for the samples after transesterification (Fig. 9D). This may be related to the replacement of glycerol by methanol in the ester molecule. Figure 9C depicts that the band at ~1100 cm^{-1} (C-O oscillations) for the biodiesel sample from synthesis 12 has an intermediate value between the oil and the other samples obtained. This can be interpreted as the result of an incomplete transesterification process for this sample. This situation could be caused, among other things, by the high acid number of the primary oil, resulting in the formation of more soaps than in the other samples.

To assess the quality of the biodiesel obtained and to confirm the effectiveness of the transesterification process, the calorific value of the reaction products and the determination of carbon and hydrogen content were conducted. A summary of the carbon, hydrogen and calorimetry determinations is presented in Table 4. Measurement errors were calculated for a 95% confidence interval (n = 2). Both the heat of combustion, carbon and hydrogen determinations show very similar results for each of the biodiesel samples, regardless of the degree of processing of the primary oil used for transesterification. The slight differences between the samples may be mainly due to the origin of the rapeseed oil, which affects the percentage content of the individual fatty acids. Measurements were made for selected samples due to the availability of product samples.

An analysis of the amount of energy used for the process was performed to determine the potential benefits associated with the choice of processing waste cooking oils in the transesterification process. The results are shown in Table 3. In an earlier study[22] a similar analysis

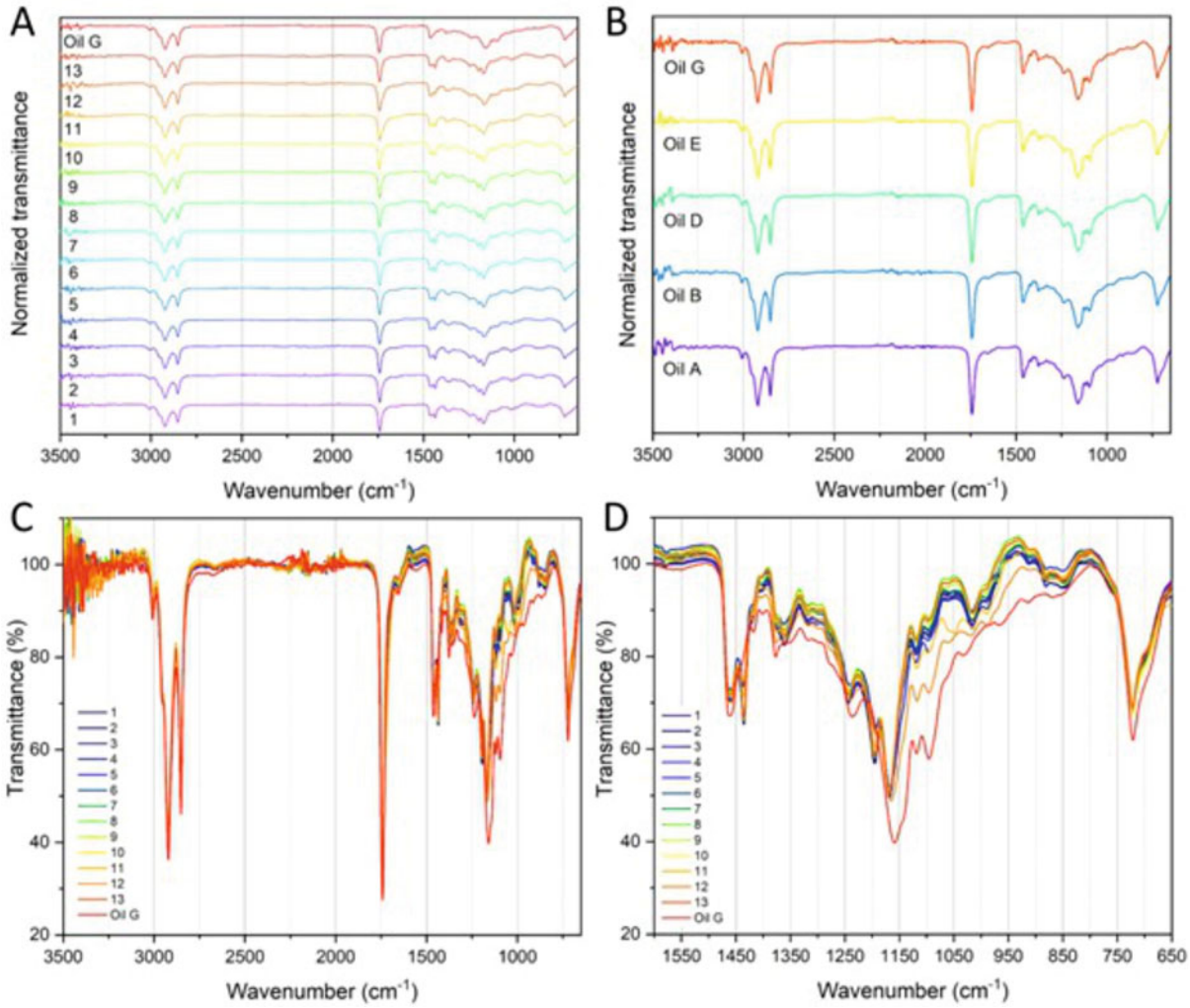


Figure 9. Normalised FT-IR spectra of the biodiesel samples (A); normalised FT-IR spectra of the waste oils used for the syntheses (B). FT-IR plot showing superimposed transmittance plots of the obtained biodiesel samples (C) and magnification of the 650–1500 cm^{-1} region (D). Oil sample G was used as the reference sample

Table 4. Statistical characteristics of input parameters used in the neural network modeling

Sample ID	HHV (MJ/kg)	LHV (MJ/kg)	C (% w/w)	H (% w/w)
10	39.8±0.2	37.0±0.4	78.7±2.2	12.4±0.8
6	39.0	36.3±0.1	80.8±2.0	12.3±0.8
7	39.6	36.9±0.3	79.5±1.2	12.6±1.0
8	39.9	37.0±0.2	82.3±1.0	13.0±0.7
9	39.7	36.7±0.6	79.2±1.7	13.9±2.4

was performed, but only for the water that was removed before transesterification, not for the entire process.

Considering energy efficiency, the most efficient method is the method no. 1 – direct transesterification (without prior FFA esterification) and heating to 60 °C. Method no. 1 should be preferred for oils with a low acid number. For oils with a higher acid number considering energy efficiency, method no. 4 with pre-esterification in the presence of cationite shall be the most effective. Method no. 3 with pre-esterification at 250 °C and 40 bar requires significantly more energy, which is not compensated for by process efficiency. It should be borne in mind that under industrial conditions, using a reactor with a volume of the order of a few hundred litres or a few thousand litres, and better thermal insulation, a higher efficiency in the use of energy consumed for the process could be achieved.

The work described above is also an example of the use of a multi-reactor laboratory system. Multi-reactor system Matrix 9 HAAS in the area of waste edible oil processing research is designed for process experiments and verification of process assumptions, enabling rapid adaptation of process configurations and parameters to different methods, scales and to work with streams with different processing step needs. Matrix9 HAAS enables multi-stage transesterification reactions to be performed in a single system with online monitoring of physicochemical parameters (temperature, pressure, etc.) and analysis of product quality before decisions are made to modify parameters or invest in an industrial-scale process line.

CONCLUSIONS

The use of waste cooking oils as feedstock for biodiesel production represents a promising and sustainable approach to waste management and alternative energy production. Through the use of automated multi-reactor Matrix 9 HAAS system, studies can be conducted to verify process parameters and performance, maximise yields and assess environmental benefits (including energy efficiency) before implementing the process on an industrial scale.

The transesterification reaction of waste rapeseed oils using four different methods yielded 13 bioester samples. The samples were subjected to FT-IR analysis, the heat of combustion was determined and the carbon and hydrogen contents were determined. During the course of the syntheses, a negative effect of the increased acid number of the oil on the efficiency of the overall process was noted. The high FFA content significantly impedes the separation of the bioester from the rest of the reaction mixture. To reduce the amount of FFA in the oil, an additional pre-processing step (FFA esterification) was used before the actual transesterification reaction. This was achieved by reacting the oils with MeOH in the presence of an acid catalyst (H2SO4 or cationite) or reacting under elevated temperature and pressure (250 °C and 40 bar). Transesterification of oils in the presence of KOH can be optimally directly applied for oils with a low acid number. While for oils with a higher acid number, an additional esterification stepis advisable in the presence of an acid catalyst to remove excess FFA. The high-temperature, high-pressure method of FFA esterification without a catalyst is an alternative solution, but its requirements for the high energy intensity of the process and a high-pressure reactor make this method sub-optimal for industrial-scale applications. Nevertheless, the potential benefits that can be derived from the management of WCO volumes, including those with high FFA content for biofuel production, still represent a significant research challenge in terms of optimising process parameters. Further work using multi-reactor systems, such as screening catalysts and assessing the real energy efficiency of these processes, is also part of the efforts in this direction.

Further investigations that can be conducted, which was not the aim of this work, are NMR spectroscopy or coupled gas chromatography - mass spectrometry (GC-MS) methods. Potential further developments of the topic discussed here are studies on various other types of waste cooking oils, and processing studies for different streams of WCO (with different degrees of proceeding) used during multi-stage transesterification.

A potential application of the research results is in the area of environmental engineering for the development and optimisation of pilot and industrial processes for the treatment of waste cooking oils as waste for use in the production of biodiesel and glycerine-based products.

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