

Influence of Reaction Parameters and Feedstock Type on the Synthesis of Fatty Acid Propyl, Butyl, Isobutyl, Pentyl, and Isopentyl Esters



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In recent decades, conventional biodiesel synthesis from methanol or ethanol and sunflower and rapeseed oil as feedstock has also introduced the use of higher and branched alcohols and the use of waste sources of triglycerides. This study examined the influence of reactant molar ratio (5:1–12:1), mass fraction of the potassium hydroxide catalyst (1–3 wt%), time (30–120 min), type of feedstock and alcohol on the conversion of fatty acid alkyl esters. The results showed that the presence of structural branching had a negative influence on the reaction conversion. Regarding the feedstocks, the highest conversions were obtained when using coconut oil rich in short-chain saturated fatty acids, while the conversions of biodiesel obtained from animal fat and unsaturated oils were lower. Molar ratio of the reactants and the mass fraction of the catalyst had the highest influence on the reaction conversion.

Keywords

biodiesel, transesterification, reaction parameters, fatty acid propyl esters, fatty acid butyl esters

Introduction

Fatty acid alkyl esters (biodiesel) are a renewable source of energy obtained through a transesterification reaction of a certain feedstock (usually vegetable oils or animal fats) with an alcohol (typically methanol or ethanol), in the presence of a catalyst (conventionally, homogeneous or heterogeneous acid/base catalysts)¹. Based on the feedstock of choice, biodiesel is categorized into different generations of biofuels. The first generation belongs to the group of edible oils (e.g., sunflower oil, rapeseed oil, coconut oil, soybean oil, palm oil, olive oil, etc.); the second generation gathers all kinds of non-edible oils (e.g., jojoba oil, castor oil, karanja oil, babassu oil, jatropha oil); the third generation focuses on waste oils (namely, waste cooking oil, animal tallow, chicken fat, poultry fat, fish oil), while the last, and the most innovative fourth generation of biodiesel belongs to so-called solar biodiesel (electrobiofuels, synthetic cell biodiesel, photobiological solar biodiesel)². The type of feedstock and alcohol selected for the biodiesel synthesis and its physical and chemical properties dictate what kind of application properties this biofuel will have³.

Feedstock properties, such as total content of free fatty acids, moisture, and other impurities, as well as the lower heating value, are some of the most important traits that depend on the chemical composition of a triglyceride source, and indicate whether this feedstock should undergo a certain pretreatment prior to being used in biodiesel synthesis. For example, if a feedstock contains a high percentage of free fatty acids (> 1 wt%), as well as water, it is prone to cause unwanted saponification reactions, and a decrease in overall conversion if using an alkaline catalyst. Waste cooking oils are especially susceptible to these changes due to the heating process they are subjected to, in which long triglyceride carbon chains break and detach from the main molecule, forming hydroscopic free fatty acids⁴.

In general, the main differences in the composition of vegetable oils and animal fats lie in the degree of saturation of their fatty acids. Vegetable oils as triglycerides, are liquid at room temperature, because they consist of unsaturated fatty acids, e.g., sunflower oil, rapeseed oil, or waste cooking oil. Coconut oil and animal fat (pork lard), for instance, are mostly composed of saturated fatty acids, which make them solids at room temperature. The average chemical structures of the aforementioned sources of triglycerides are given in Fig. 1, whereas the main

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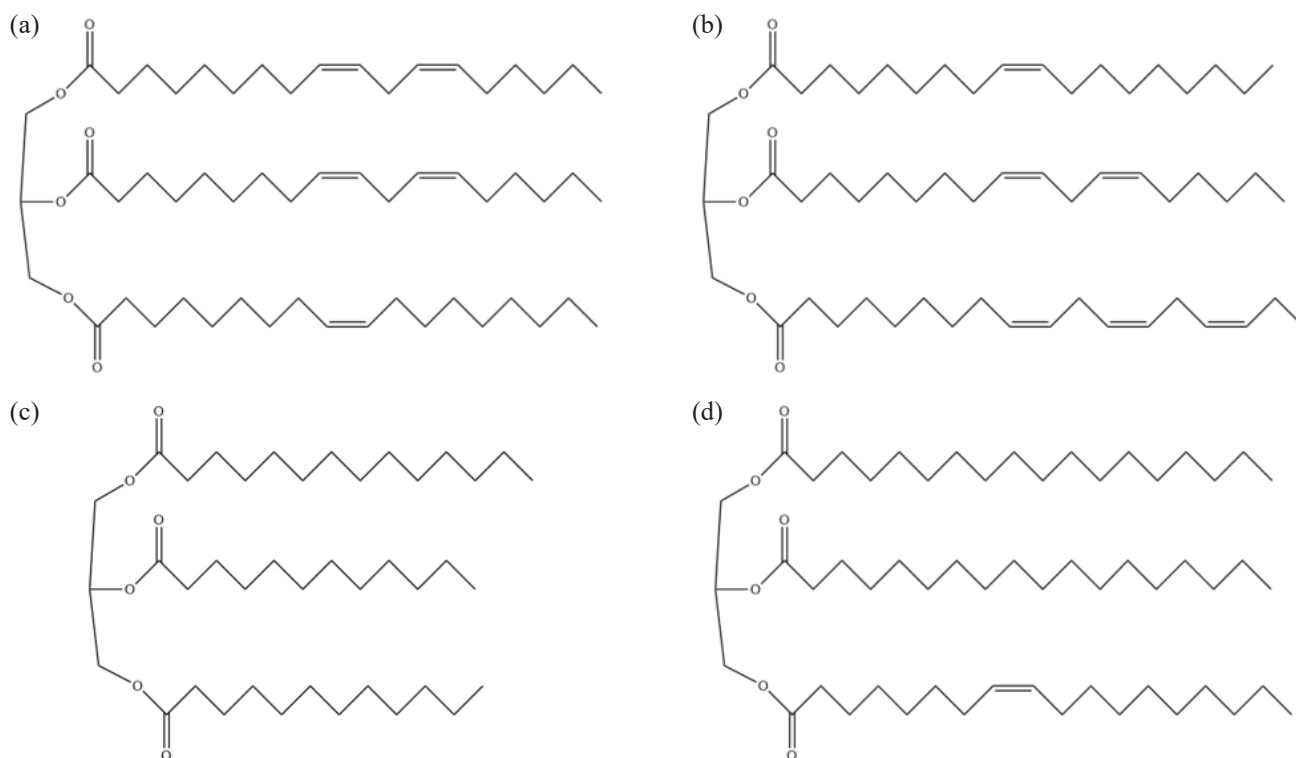


Fig. 1 – Average structural formulas of different feedstocks: (a) sunflower oil/waste cooking oil, (b) rapeseed oil, (c) coconut oil, (d) and animal fat

Table 1 – Main acidic constituents in different types of feedstock

Feedstock	Main constituents (wt%)
Sunflower oil ⁵	Linoleic acid (52.34) Oleic acid (22.52)
Rapeseed oil ⁵	Oleic acid (62.0–77.8) Linoleic acid (14.1–32.0)
Coconut oil ⁶	Lauric acid (40.0–50.0) Myristic acid (15.0–20.0)
Waste cooking oil ⁵	Oleic acid (38.6–44.7) Linoleic acid (32.8–36.0)
Animal fat ⁷	Palmitic acid (23.7) Stearic acid (12.9)

constituents in feedstock composition are presented in Table 1.

When it comes to the alcohols used in biodiesel synthesis, this paper focuses on the use of higher and branched alcohols, i.e., 1-propanol, 1-butanol, isobutanol, 1-pentanol, and isopentanol.

Finally, the choice of the reactants for the transesterification reaction needs to be followed by the appropriate choice of reaction parameters (reaction temperature, time, molar ratio of reactants, and mass fraction of catalyst). Literature suggests that increasing the molar ratio of alcohol to oil/fat leads

to an increase in the conversion of, e.g., conventional fatty acid methyl esters, while an increase in the mass fraction of a homogeneous catalyst (usually sodium or potassium hydroxide) increases the reaction conversion to a certain extent, whereas the use of a heterogeneous catalyst results in a continuous rise in the reaction conversion⁵. Furthermore, one of the studies of Likozar *et al.*⁶ investigated the effect of process conditions on equilibrium, reaction kinetics, and mass transfer for triglyceride transesterification of canola oil with methanol to biodiesel. The authors tested the influence of different alcohol to oil ratios of 1:3, 1:4, 1:5, 1:6, 1:7, and 1:8 (mol mol⁻¹), with potassium hydroxide as a catalyst (0.2, 0.4, 0.6, 0.8, 1.0, or 1.2 wt%), through different reaction times, 25–75 min (depending on the process conditions), as well as a variety of temperatures; 30, 40, 50, 60, and 70 °C; and rotational speeds, 100–600 rpm, on the conversion of transesterification reaction. Their experimental results suggested that the increase in the values of all of these parameters within the investigated range led to an increase in the reaction conversion⁶. Another study of Likozar *et al.*⁷ also investigated the influence of the reaction parameters on the same reaction system; however, this time via continuous 18 mL (5-millimeter internal diameter) tubular reactor with static mixers. Varied parameters were temperature 30, 40, 50, 60 or 65 °C, and 0.2, 0.4, 0.6, 0.8, 1.0 or 1.2 wt% (per oil weight) based on concentrations of catalyst potassium hydroxide, while the reactions lasted up to

an hour. Results showed that again higher temperatures favored the transesterification reaction, since, e.g., at 65 °C, the biodiesel conversion was 70 %, whereas the temperature of 30 °C resulted in a conversion of only 5 %. Other parameters, such as molar ratio of methanol to oil, indicated that, in this continuous process, the conversion would increase to a certain point (molar ratio of 4:1), where it reached a plateau, i.e., increasing excess in alcohol would not have an influence on the conversion of methyl esters. The addition of catalyst, however, continuously displayed a positive effect on the reaction conversion, the highest one being achieved with 1.2 wt% of potassium hydroxide⁷. Moreover, *Klofutar et al.*⁸ considered how the reaction parameters influenced biodiesel conversion if waste feedstock, i.e., waste sunflower oil, had been employed in the synthesis. They used a combination of size-exclusion chromatography and ¹H NMR to quantitatively monitor the transesterification reaction, that is the formation of diglycerides, monoglycerides, and methyl esters from the starting triacylglycerols. The parameters kept constant were the rotational speed of mechanical stirrer of 500 rpm, and an alcohol to oil molar ratio of 6:1. The results showed that, after 16 minutes of the reaction, the conversion was 64 wt% at 40 °C, and 89 wt% at 50 °C. After 90 min, the biodiesel conversion surpassed 86 wt%⁸. Waste frying oil was also used in the study of *Uzun et al.*⁹, in which they optimized the reaction parameters, e.g., temperature, reaction time, catalyst concentration, methanol/oil molar ratio, or catalyst type (sodium hydroxides, methoxides, and ethoxides), to obtain high biodiesel conversions. Their results showed that the optimal conditions for achieving 97 % of purified ester content were 0.5 wt% of NaOH, reaction time of 30 min, at temperature of 50 °C, and methanol to oil ratio of 7.5. Due to high hygroscopicity of sodium hydroxide, increasing the amount of the catalyst and reaction time made saponification and hydrolysis reactions more probable, thus decreasing the biodiesel conversion. In addition, at reactant molar ratios higher than 7.5, excess methanol increased glycerol's solubility in the ester phase, leading to its interference with the oil conversion to biodiesel, and formation of foam. Lastly, if the temperatures were higher than 50 °C (near or above methanol's boiling point), the rate of the saponification of triglycerides would exceed the rate of alcoholysis, which resulted in lower conversions⁹.

Therefore, the goal of this study was to investigate how reaction systems containing higher (C₃-C₅) and branched alcohols and feedstocks of different composition in the presence of homogeneous alkaline catalyst, potassium hydroxide, behave under different experimental conditions.

Experimental

Materials

Selected feedstocks for biodiesel synthesis were sunflower oil (ZVIJEZDA plus d.o.o.), rapeseed oil (Denntree), coconut oil (Nutrigo), animal fat (PPK Karlovačka mesna industrija d.d.), and waste cooking oil (sampled from student's canteen Studentski centar Savska cesta 25, total acidity of 1.19 mg KOH g⁻¹ (ASTM D 664:2018), and water content of 0.069 wt% (HRN EN ISO 12937:2001).

Alcohols used in the synthesis were 1-propanol (99.7 %, Lach-Ner, water content ≤ 0.1 %), 1-butanol (99.5 %, Carlo Erba Reagents, water content ≤ 0.1 %), isobutanol (> 99 %, Lach-Ner, water content ≤ 0.05 %), 1-pentanol (99.8 %, Lach-Ner, water content ≤ 0.1 %), and isopentanol (98.5 %, VWR LIFE SCIENCE, water content ≤ 0.3 %). Potassium hydroxide (min 89.5 %, GRAM-MOL d.o.o.) was used as catalyst and dried at a temperature of 100 °C for 30 minutes before use.

Experimental plan

Experiments were conducted according to the experimental plan presented in Table 2, under different combinations of reaction times (30–120 min), molar ratios of reactants (5:1–12:1), and mass fractions of catalyst (1–3 wt%), at a constant temperature of 60 °C.

Biodiesel synthesis and conversion analysis

Each biodiesel was synthesized using 20-milliliter glass tubes dipped in an oil bath and mixed with a magnetic stirrer. Ahead of synthesis, reactants were weighed in two separate glass tubes, one containing triglyceride of choice, and the other containing potassium hydroxide dissolved in a selected alcohol. Both tubes were put into the bath and warmed up to the temperature of 60 °C. Immediately after they were heated at given temperature, their contents were mixed together, capped, and put back into the bath for the time remaining. A milliliter of sample for ¹H NMR (proton nuclear magnetic resonance) analysis was taken after 30, 60, and 120 minutes through the sealed tube cap punctured with a syringe needle, and then immediately quenched in an ice bath to terminate the reaction after each time interval. Samples remained frozen until NMR measurements using Bruker Avance instrument, at 300 MHz, with a solvent deuterated chloroform (CDCl₃). These measurements allowed the conversion to be calculated using the equation described by *Faraguna et al.*¹⁰

$$\text{Conversion, \%} = \frac{\text{Surface area at around 4.0 ppm}}{\text{Surface area at around 2.3 ppm}} \cdot 100 \quad (1)$$

Table 2 – Combination of the reaction parameters selected for the synthesis of fatty acid propyl, butyl, isobutyl, pentyl and isopentyl esters (A – alcohol, O – oil/fat)

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)
Sunflower oil/ Rapeseed oil/ Coconut oil/ Animal fat/ Waste cooking oil	1-Propanol		5	1
			5	3
			10	1
			10	3
	1-Butanol		5	1
			5	3
			10	1
			10	3
	Isobutanol	2*	5	1
			5	3
			10	1
			10	3
Isopentanol	5*	6	1	
		6	3	
		12	1	
		12	3	
	15*	6	3	
		30	1	
		30	1	
		60	3	
	120	5	1	
		5	3	
		12	1	
		12	3	

* applied only in the synthesis of fatty acid pentyl esters

In Equation 1, surface area around 4.0 ppm is obtained by integrating signals (here, triplets) that belong to the synthesized fatty acid alkyl esters (desired products). On the other hand, surface area around 2.3 ppm is a result of integration of all the signals that belong to the used triglyceride source, byproducts (diglycerides and monoglycerides), as well as the obtained esters.

Results and discussion

Reaction conversions calculated for each experiment using Eq. 1 are presented in Tables S1-5 (see Supplement). The dependence of the conversion of each biodiesel from selected feedstock on the mass fraction of KOH and corresponding alcohol to oil ratio after 120 minutes, as well as on time with a lower and higher value of the reactant ratios is presented in Figs. 1–6. For all investigated systems during and after the synthesis, one-phase systems were obtained and no glycerol phase separation was observed.

Influence of the parameters and feedstock type on the reaction conversion of fatty acid propyl esters

Synthesis of fatty acid propyl esters (FAPRE) was conducted using one of the following feedstocks (given in different colors in Fig. 2): sunflower oil (a-c), rapeseed oil (d-f), coconut oil (g-i), and animal fat (j-l).

The results shown in the first column of Fig. 2 indicate that the increase in the molar ratio of the reactants and the mass fraction of the catalyst resulted in an increase in the reaction conversion. When the molar ratio of 1-propanol to sunflower oil was kept at a lower value of 5:1, the increase in mass fraction of KOH from 1 to 3 % resulted in a conversion increase of 36.0 %. However, the same change caused the conversion to increase by only 7.0 % when the reactant molar ratio was kept at a higher value of 10:1. Furthermore, keeping the mass fraction of KOH at a constant value of 1 %, while increasing the reactant molar ratio from 5:1 to 10:1, resulted in a conversion jump by 40.0 %. This change is far less significant at 3 wt% of KOH, leading conversion to increase by only 7.0 %. With rapeseed oil used as feedstock for FAPRE synthesis, the obtained conversion results showed that the molar ratio of the reactants was a more significant parameter to the reaction conversion than the mass fraction of the catalyst. Specifically, after 120 minutes, with an increase in molar ratio of reactants from 5:1 to 10:1, the reaction conversion increased by 30.0 % (with 1 wt% of KOH) or 36.0 % (with 3 wt% of KOH). However, an increase in catalyst mass fraction from 1 to 3 % would only result in a conversion increase of 6.0 % (at alcohol to oil ratio of 5:1) or 11.0 % (at alcohol to oil ratio of 10:1). Compared to the results with sunflower oil, the influence of KOH mass fraction on the conversion of FAPRE was less pronounced at lower molar ratio of 5:1.

Compared to FAPRE from sunflower and rapeseed oil, the overall conversion of FAPRE was higher when using coconut oil (Fig. 2g). In addition, significant conversion changes were visible only in the case of increasing the reactant molar ratio from 5:1 to 10:1 at the lower value of catalyst mass fraction of 1 %. Here, conversion increased by 15.0 %. The behavior of the reaction system containing alcohol 1-propanol and animal fat as a renewable source, in the presence of the catalyst KOH, was similar to sunflower oil and rapeseed oil in terms of conversion when the reaction parameters were changed. The main difference lies in the significance that increasing the catalyst mass fraction from 1 to 3 % had on the conversion at the reactant molar ratio of 5:1. After 120 minutes, the increase in catalyst mass fraction led to an increase in

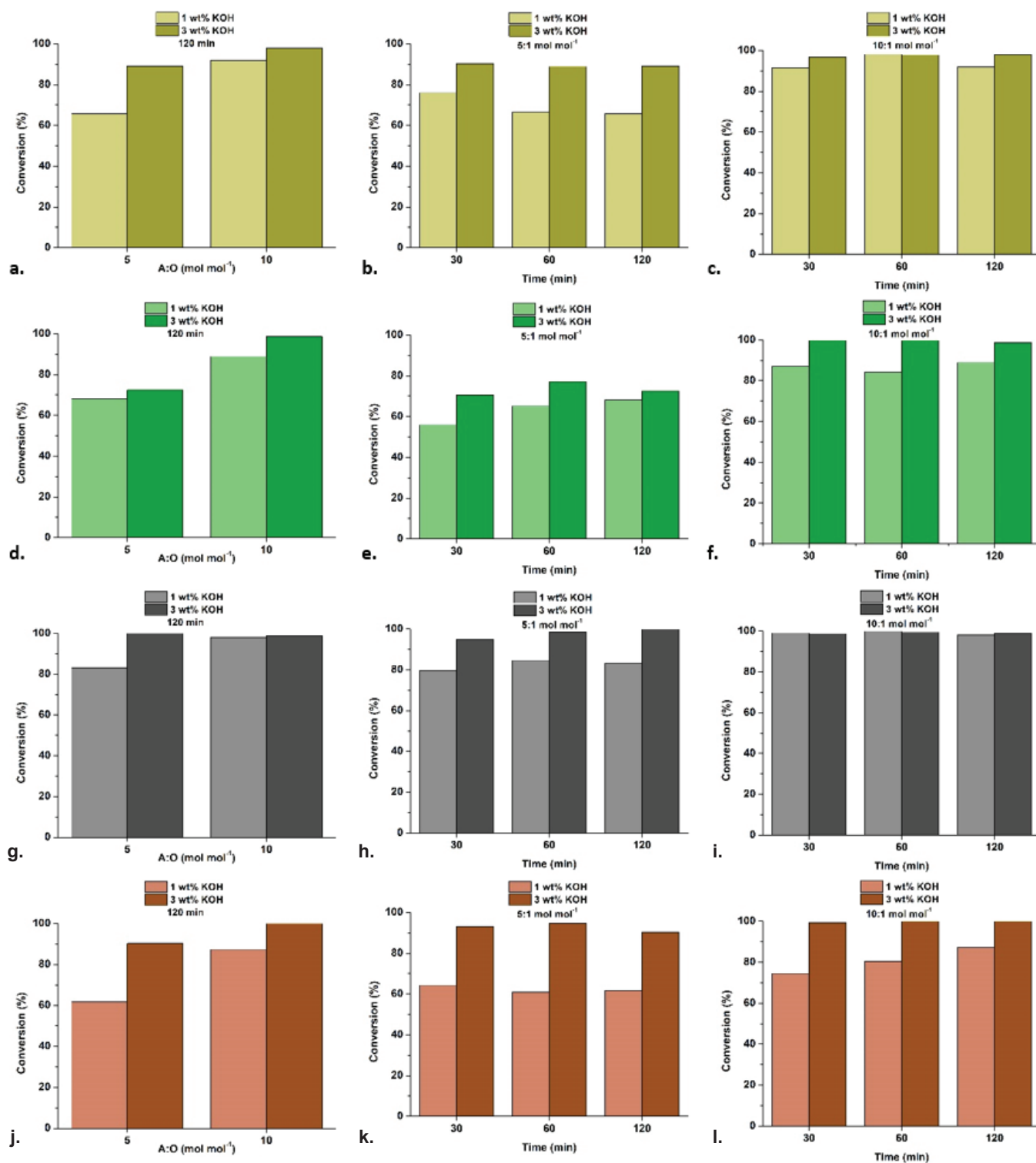


Fig. 2 – Dependence of the conversion of FAPRE from sunflower oil (1st row), rapeseed oil (2nd row), coconut oil (3rd row), and animal fat (4th row) on the mass fraction of KOH and: 1-propanol to oil ratio after 120 minutes (1st column); time with the reactant ratio of 5:1 mol mol⁻¹ (2nd column); time with the reactant ratio of 10:1 mol mol⁻¹ (3rd column)

conversion of 28.0 and 13.0 % at a molar ratio of 5:1 and 10:1, respectively. As evident from the second and third columns of Fig. 2, reaction time was less important for the conversion than the catalyst mass fraction. In addition, the influence of time becomes increasingly insignificant as the other reaction parameters approach their maximum values. In

the case of sunflower oil, the influence of both time and catalyst mass fraction was more prominent at the lower value of reactant ratio of 5:1. Here, the addition of catalyst caused the conversion to increase by 18.6, 33.8, and 35.7 % after 30, 60, and 120 minutes, respectively, whereas the same change at a higher molar ratio of 10:1 led to a conversion

increase of only 5.7 %, 0.4 %, and 6.6 %. When using rapeseed oil for the synthesis, at the lower reactant ratio of 5:1, the increase in KOH mass fraction resulted in a conversion rise of 26.0 % (after 30 min), 18.0 % (after 60 min), and 6.5 % (after 120 min). At a ratio of 10:1 mol mol⁻¹, the same will result in a conversion increase of 15.0 %, 19.0 %, and 11.0 %, after 30, 60, and 120 minutes, respectively. With coconut oil, the influence of time was also more pronounced only when the reactants molar ratio was set to 5:1. Increasing the molar ratio resulted in a reaction system where conversion hardly changed with time, i.e., reached a value of 99.0 % after only 30 minutes. Moreover, the highest increase in the reaction conversion of 19.1 %, with the increase in molar reactant ratio from 5:1 to 10:1, occurred after 30 minutes when the value of catalyst mass fraction was at 1 %. When this value was higher (3 %), the same change resulted in an increase of only 3.9 % after the same period. On the other hand, biodiesel from animal fat achieved conversion values of 93.1 % and higher after only 30 minutes. In addition, the increase in the molar ratio from 5:1 to 10:1 resulted in a conversion increase of 25.5 %, with 1 wt% of KOH, whereas the change in the same parameter caused conversion to increase by 9.7 %, with 3 wt% of KOH.

Overall, the highest experimental conversion values were achieved in the cases of sunflower oil, rapeseed oil, and animal fat, obtained at reactant molar ratio of 10:1 and catalyst mass fraction of 3 %, after one hour. When using coconut oil as feedstock, the highest conversion can be obtained either at a higher molar ratio of 10:1, and with 1 wt% of KOH, after only 60 minutes, or at a lower molar ratio of 5:1, but using more catalyst (3 wt%), and conducting the reaction over a period of 120 minutes.

Influence of parameters and feedstock type on the reaction conversion of fatty acid butyl esters

Fatty acid butyl esters (FABE) were synthesized using sunflower oil, rapeseed oil, coconut oil, and animal fat as feedstock, presented in Fig. 3.

As evident from Fig. 3, a and d, no matter what oil was used (sunflower or rapeseed oil) or alcohol (1-propanol or 1-butanol), the parameters of the transesterification reaction after 120 minutes had a similar influence on the reaction conversion. The increase in reactant molar ratio and catalyst mass fraction had a positive effect on the reaction conversion. For instance, at 1 wt% of KOH, increasing the molar ratio from 5:1 to 10:1 resulted in a conversion jump of 47.0 %. The same caused conversion to rise by 12.0 %, at a mass fraction of KOH of 3 %. Also, maintaining the molar ratio at a constant value of 5:1, and increasing the mass fraction from

1 to 3 %, resulted in a conversion increase of 33.0 %, whereas the same led to a conversion increase of only 1.0 %, when the molar ratio was kept at a higher value (10:1). In the case of rapeseed oil, after 120 minutes, at constant molar ratio values of 5:1 and 10:1, when the KOH mass fraction was increased from 1 to 3 %, the reaction conversion increased by 6.4 % and 8.2 %, respectively. At constant KOH mass fraction values, when the reactant molar ratio was changed from 5:1 to 10:1, the reaction conversion increased by 17.1 % and 18.9 %, respectively. The latter leads to the conclusion that the reactant molar ratio was more significant as a reaction parameter on FABE conversion than catalyst mass fraction, whether the feedstock was sunflower or rapeseed oil. Fatty acid butyl esters synthesized from coconut oil showed high conversion values (95.0 % and higher, Fig. 7a), after 120 min, even at lower values of reactant molar ratio and catalyst mass fraction. Therefore, the increase in these two reaction parameters had no significant influence on the increase of reaction conversion. This is unlike any other previously described reaction system, even those with the same oil, just with different alcohol (1-propanol), meaning that the transesterification of coconut oil is better with 1-butanol than with 1-propanol. When animal fat was used as feedstock for FABE synthesis, the results showed that, at a higher reactant molar ratio (10:1), the influence of increasing the KOH mass fraction from 1 to 3 % was insignificant.

In terms of reaction kinetics, time in each reaction system shown in Fig. 3 had a positive effect on the conversion only at 3 wt% of KOH. In addition, regardless of time, an increase in KOH mass fraction will always lead to at least a slight increase in the reaction conversion of FABE from rapeseed oil. This similarity holds true for FAPREs synthesized using sunflower oil or rapeseed oil. In the case of sunflower oil, the conversion decreased ever so slightly over time with 1 wt% of KOH, and molar ratio of 10:1. However, at lower values of catalyst mass fraction, and reactant molar ratio, conversions tended to drop over time in the sunflower oil systems with both 1-propanol and 1-butanol. When using rapeseed oil, at reactant molar ratio of 5:1, a higher catalyst fraction prompts the conversion to rise by 8.7 %, 13.0 %, and 8.6 %, after 30, 60, and 120 minutes, respectively. When this ratio was at 10:1 mol mol⁻¹, conversion increased by 5.6 % after 60, and by 8.2 % after 120 minutes. In the case of coconut oil, FABE conversions followed a similar trend to those of FAPRE, i.e., the increase in catalyst mass fraction, especially at lower molar ratio value of 5:1, caused reaction conversion to increase at all times, and throughout the reaction. The increase in KOH mass fraction from 1 to 3 % caused

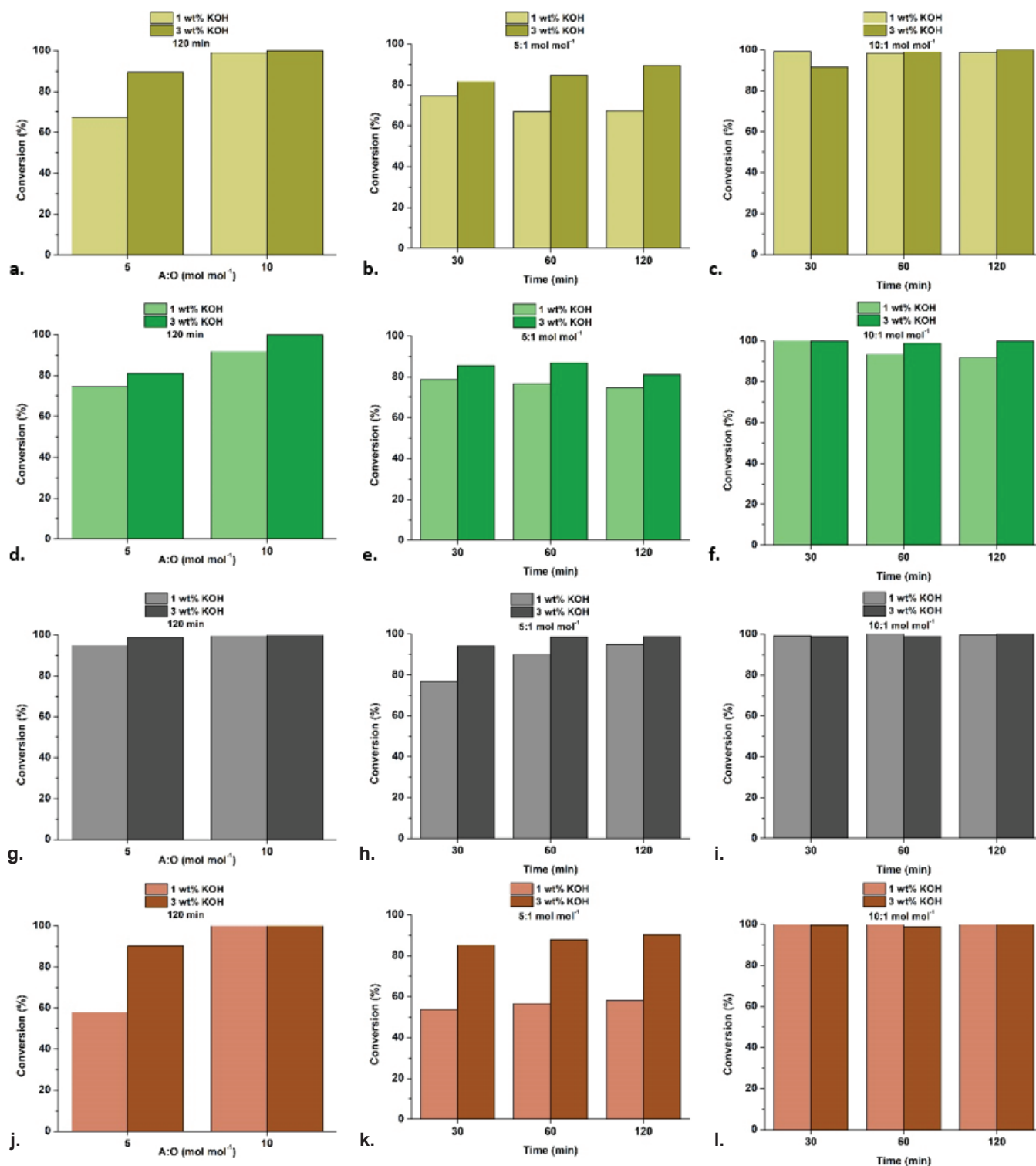


Fig. 3 – Dependence of the conversion of FABE from sunflower oil (1st row), rapeseed oil (2nd row), coconut oil (3rd row), and animal fat (4th row) on the mass fraction of KOH and: 1-butanol to oil ratio after 120 minutes (1st column); time with the reactant ratio of 5:1 mol mol⁻¹ (2nd column); time with the reactant ratio of 10:1 mol mol⁻¹ (3rd column)

the conversion to increase by 17.4 % after 30 minutes of synthesis. The increase in the molar ratio of 1-butanol to coconut oil from 5:1 to 10:1 achieved a conversion increase of 22.3 %, again within the first 30 minutes of the reaction. At a higher value of the reactant molar ratio, the influence of time was insignificant to the already high reaction conversion

of 99.1 %, achieved after only 30 minutes with 1 wt% of KOH. The same applies to the systems with animal fat, where a total conversion was achieved after only 30 minutes of the reaction catalyzed by 1 wt% of KOH, and remained constant over time. This is the main difference from the reaction system with 1-propanol, where regardless of the reactant

molar ratio, the increase in KOH mass fraction had a significant, positive influence on the reaction conversion. Thus, at the lower reactant molar ratio of 5:1, the presence of a higher KOH mass fraction in the system caused the conversion to increase by 31.4 %, 31.2 %, and 32.3 % after 30, 60, and 120 minutes, respectively. However, compared to the corresponding FABE conversions from, e.g., coconut oil, all of these conversion values were lower at a molar ratio of 5:1.

Comparing these systems to those that already exist in the literature, for example, the research of Kumar *et al.*¹¹, where authors conducted an optimization of transesterification of non-edible mahua oil with 1-butanol, in the presence of the same catalyst, potassium hydroxide, the conversions of our biodiesel are overall higher. The optimal yield value in their system was 94.8 %, at temperature of 80 °C, after 90 min, with a molar butanol to oil ratio of 6:1, and 1.5 wt% of potassium hydroxide. In addition, Kumar *et al.* concluded that the increase in molar ratio of butanol to mahua oil above 8:1 and/or the increase in KOH mass fraction above 1.5 % resulted in a decrease in the butyl esters yield, due to the occurrence of side reactions (water formation, saponification). In contrast, our findings showed an opposite trend, which may be attributed to the low water content in our 1-butanol (≤ 0.1 %), and complete drying of potassium hydroxide prior to the reactions.

In summary, a 100.0 % conversion of FABE was achieved in all cases at a 1-butanol to triglyceride molar ratio of 10:1, with a difference that, in the case of sunflower oil, the reaction needs to be led for two hours, with 3 wt% of KOH; in the case of rapeseed oil, the reaction took 30 minutes, and 1 wt% of KOH; in the case of coconut oil, there were two possible parameter combinations to achieve total conversion, i.e., either with 1 wt% of KOH, after 60 minutes, or with 3 wt% of KOH, after 120 minutes; in the case of animal fat, only 30 minutes with 1 wt% of KOH were needed to convert 100.0 % of fat to FABE.

Influence of the parameters and feedstock type on the reaction conversion of fatty acid isobutyl esters

Sunflower oil, rapeseed oil, coconut oil, and animal fat were chosen as feedstock in the synthesis of fatty acid isobutyl esters (FAIBE, Fig. 4).

Using a branched butanol isomer, instead of a straight-chained isomer, in transesterification of selected triglyceride sources generally results in their lower conversion to alkyl esters (see Supplement, Table S1). To achieve conversion values close to those of FABE, more severe reaction conditions needed to be applied, i.e., the lower level of reactant

molar ratio was increased from 5:1 to 6:1, and the highest level was increased from 10:1 to 12:1. In terms of the trends in the conversion values due to parameter changes, no major difference was observed, i.e., the increase in reactant molar ratio and catalyst mass fraction led to the increase in reaction conversion. The higher molar ratio of the alcohol to oil/fat led to lower viscosity and improved miscibility, resulting in a chemical equilibrium shift towards the reaction products, i.e., higher biodiesel conversion. Numerous similar examples of transesterification reactions were reviewed in a paper by Jin-Suk *et al.*¹², where they emphasized how the increase in the reactant molar ratio caused the conversion to reach a certain level, after which it continued to stagnate. Our results also showed that at higher molar ratios, the influence of catalyst mass fraction became less prominent, meaning that the most significant reaction parameter was the reactant molar ratio, followed by catalyst mass fraction, while the least significant was reaction time. The conversion of fatty acid isobutyl esters (FAIBE) was in some cases slightly higher when using rapeseed oil as feedstock, compared to sunflower oil. Furthermore, compared to fatty acid butyl esters synthesized from coconut oil, where after 120 minutes all three observed reaction parameters had little to no influence on the reaction conversion, here a visible change in the conversion was observed, especially at the lower molar ratio value of 6:1. In addition, compared to FABE, all the conversions of FAIBE from coconut oil had lower values. The results gathered in a research conducted by Leung *et al.*¹³ with neat and used frying oil are in agreement with the ones presented here, that is, the increase in catalyst mass fraction led to an increase in reaction conversion. Finally, when animal fat was combined as a reactant in a transesterification with isobutanol, in the presence of KOH, the obtained FAIBE conversions at all parameter levels were lower than those obtained when a straight-chain butanol isomer was used. When the molar ratio increased from 6:1 to 12:1, at 1 wt% of KOH, the reaction conversion increased by 43.4 % after 120 minutes, but when the same occurred at catalyst mass fraction value of 3 %, the conversion increased by only 25.3 %.

In regards to the influence of the reaction time on the reaction conversion, again it is possible to state that influence is minor to none in all observed reaction systems, i.e., as a parameter it is insignificant compared to the reactant molar ratio or the catalyst mass fraction. Moreover, the positive effect that the higher reactant molar ratio has on the reaction conversion of biodiesel was also studied by Phan *et al.*¹⁴, where they used waste cooking oils. Here, as well, time had no significance on the reaction conversions, e.g., when the molar ratio of

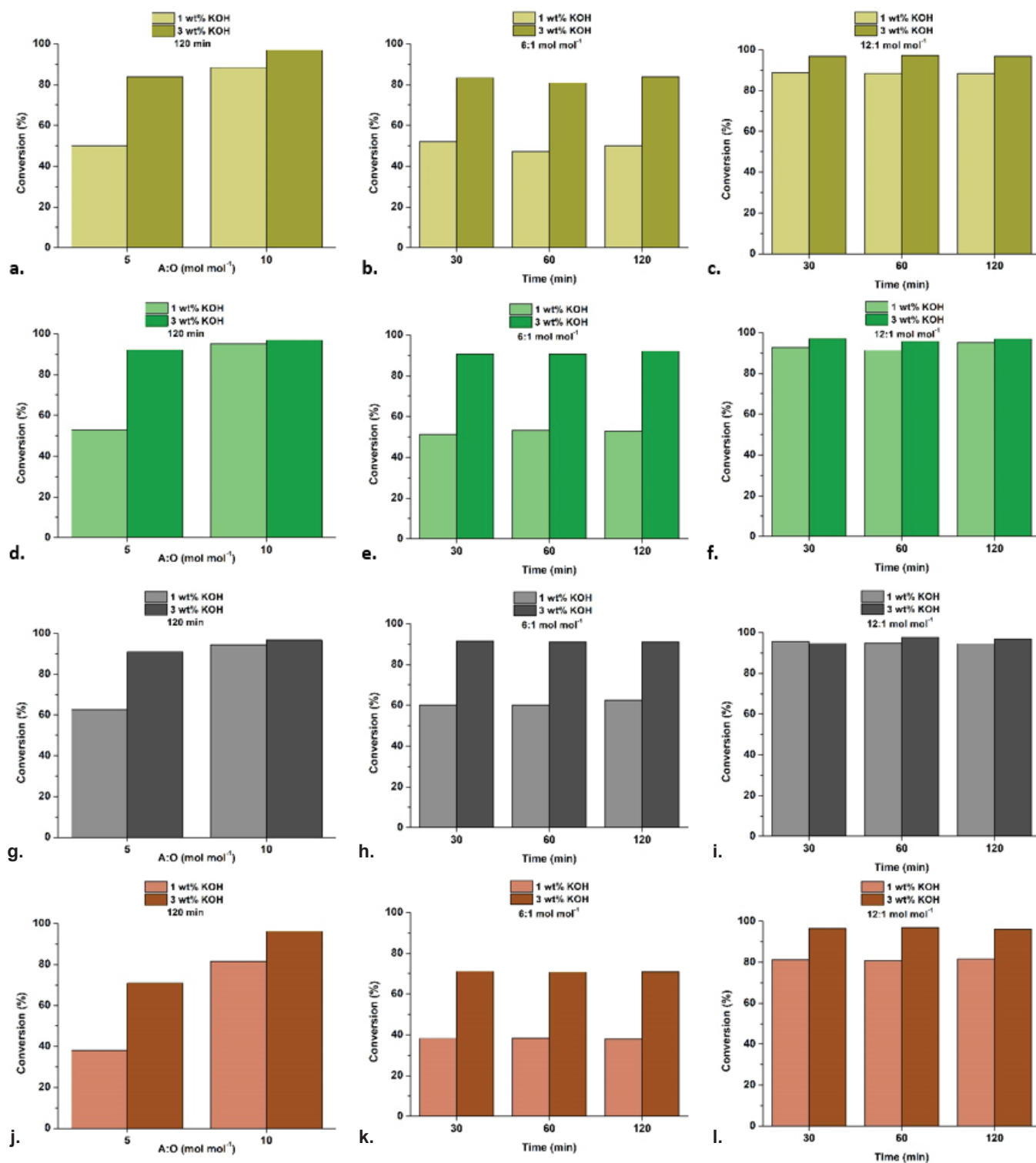


Fig. 4 – Dependence of the conversion of FAIBE from sunflower oil (1st row), rapeseed oil (2nd row), coconut oil (3rd row), and animal fat (4th row) on the mass fraction of KOH and: isobutanol to oil ratio after 120 minutes (1st column); time with the reactant ratio of 6:1 mol mol⁻¹ (2nd column); time with the reactant ratio of 12:1 mol mol⁻¹ (3rd column)

isobutanol to coconut oil was 6:1, with the KOH mass fraction of 3 %, the obtained conversion values were 91.5, 91.0, and 91.0 %, after 30, 60, and 120 minutes, respectively. In the case of animal fat, the conversion values at each reactant molar ratio and catalyst mass fraction level varied up to only 0.7 %. Keeping in mind that the accepted result de-

viation due to the repeatability of the method is 2 %, all these values are basically the same. The latter was confirmed in the study by Sanli *et al.*¹⁵, where they used different alcohols and catalysts to produce biodiesel from different vegetable oils, and concluded that, after a certain time, no rise in the transesterification conversion was observed.

The highest experimental conversion values of FAIBE when using sunflower oil (97.3 %), rapeseed oil (97.0 %), coconut oil (97.7 %), and animal fat (96.9 %) were all obtained at the isobutanol to oil/fat molar ratio of 12:1, with 3 wt% of KOH. All reactions took 60 minutes to complete, except that with rapeseed oil, which took 30 minutes.

Influence of the parameters and feedstock type on the reaction conversion of fatty acid pentyl esters

Sunflower oil, rapeseed oil, coconut oil, and animal fat were transesterified with alcohol 1-pentanol to yield fatty acid pentyl esters (Fig. 5).

The influence of the reaction parameters on the synthesis of fatty acid pentyl esters (FAPE) was in agreement with the previously mentioned cases. The increase in the reactant molar ratio and the catalyst mass fraction generally led to an increase in reaction conversion. Furthermore, the influence of the catalyst mass fraction on the reaction conversion was only noticeable at lower molar ratio values; otherwise, it became insignificant. Out of all the presented reaction systems, the latter was the most noticeable when using animal fat as feedstock, due to the rise in the reaction conversion by 34.7 %, whereas the system with coconut oil lacked this influence the most, with conversion increasing by only 17.1 %. Nevertheless, as evident from Fig. 5, a certain level of conversion was reached within 5 minutes of each reaction, and continued stagnating throughout the reaction.

Moreover, when focusing on the reaction kinetics, time influenced the increase in reaction conversion solely when the reactant molar ratio was kept at a lower value of 5:1. The influence of time was mostly visible when using coconut or rapeseed oil, and almost non-detectible when using sunflower oil or animal fat. The highest conversion through the entire time were obtained in the system with coconut oil, and the lowest in the system with animal fat.

Therefore, the highest obtained conversion when using coconut oil (100.0 %) was achieved after only 2 minutes, with reactant molar ratio of 5:1, and catalyst mass fraction of 3 wt%. At a molar ratio of 12:1 and catalyst mass fraction of 1 wt%, the highest conversion with sunflower oil was achieved after 2 minutes (100.0 %), with animal fat after 30 minutes (100.0 %), and with rapeseed oil after 15 minutes of the reaction (99.7 %).

Influence of the parameters and feedstock type on the reaction conversion of fatty acid isopentyl esters

Finally, branched alcohol isopentanol was used with sunflower oil, rapeseed oil, coconut oil, and

animal fat in the synthesis of fatty acid isopentyl esters (Fig. 6).

The significance of the reaction parameters in the synthesis of fatty acid isopentyl esters (FAIPE) from sunflower oil, rapeseed oil, coconut oil, and animal fat decreased in the following order: from reactant molar ratio, to catalyst mass fraction, and finally to reaction time. The increase in the molar ratio and the KOH mass fraction in these systems resulted in a conversion increase as well. Out of all the investigated reaction systems with sunflower oil, the lowest conversions were obtained using isopentanol as an alcohol in the synthesis, throughout the entire studied range of the selected reaction parameters. Similar conclusions were found in the study of Likozar *et al.*¹⁶, in which they synthesized biodiesel from various feedstock and alcohols with different chain lengths, and found that the increase in the linear alkyl chain resulted in a decrease in the conversion of corresponding alkyl esters. Moreover, they noticed the drop in biodiesel conversions obtained from *tert*-butanol, isopropanol, methanol, ethanol, and butanol, respectively. In addition, two reaction parameters became insignificant when 3 wt% of KOH was used in the FAIPE synthesis from sunflower oil, those being the reactant molar ratio and the reaction time. Although they are the same when it comes to trends in the reaction parameters, FAIPE and FAIBE obtained from coconut oil have quite different conversion values. The conversion values for FAIPE across all parameter levels were lower than were those of FAIBE.

Unlike other feedstock types used in FAIPE synthesis and described so far, the reaction systems with animal fat exude different conversion responses to the changes in reaction parameters. As shown in Fig. 6h, after 120 minutes of the reaction, the changes in the KOH mass fraction ceased to have significant influence on the change in the reaction conversions. This was particularly noticeable at the higher reactant molar ratio of 12:1.

When it comes to the highest experimental conversion values of FAIPE obtained in these different systems, the systems with sunflower oil and rapeseed oil had in common both the value of the reactant molar ratio (12:1) and the catalyst mass fraction (3 %). However, with sunflower oil, the conversion of 81.1 % was achieved after one hour, whereas with rapeseed oil, a slightly higher conversion of 82.4 % was achieved after only 30 minutes. The highest FAIPE conversion of 84.9 %, when using coconut oil as feedstock, occurred after 60 minutes, at a reactant molar ratio of 6:1, and a catalyst mass fraction of 3 %. The highest conversion of FAIPE from animal fat of 82.7 % was obtained after half an hour, at a molar ratio of alcohol to fat of 12:1, and a KOH mass fraction of 1 %.

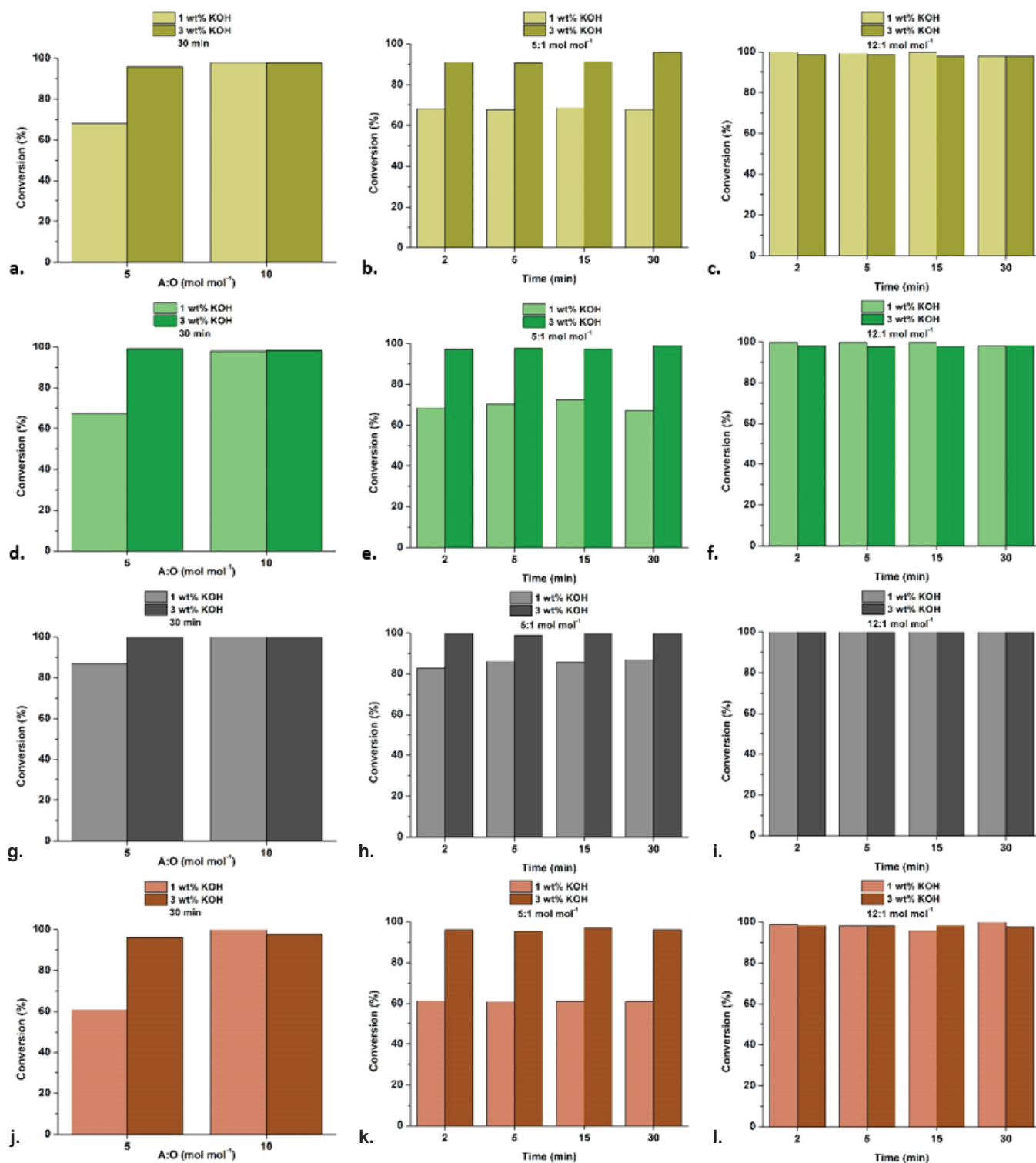


Fig. 5 – Dependence of the conversion of FAPE from sunflower oil (1st row), rapeseed oil (2nd row), coconut oil (3rd row), and animal fat (4th row) on the mass fraction of KOH and: 1-pentanol to oil ratio after 30 minutes (1st column); time with the reactant ratio of 5:1 mol mol⁻¹ (2nd column); time with the reactant ratio of 12:1 mol mol⁻¹ (3rd column)

Influence of the parameters on the reaction conversion of fatty acid isobutyl, pentyl and isopentyl esters from waste cooking oil

Synthesis of fatty acid isobutyl, pentyl, and isopentyl esters was also conducted using waste cooking oil (Fig. 7).

The use of waste cooking oil in the synthesis of FAIBE, FAPE, and FAIPE, revealed that the conversion values of FAIBE from waste cooking oil are the closest to those of FAIBE obtained from sunflower oil, with the exception of the values obtained with the molar ratio of 6:1, and KOH mass fraction of 3 %. With sunflower oil, these conversion values

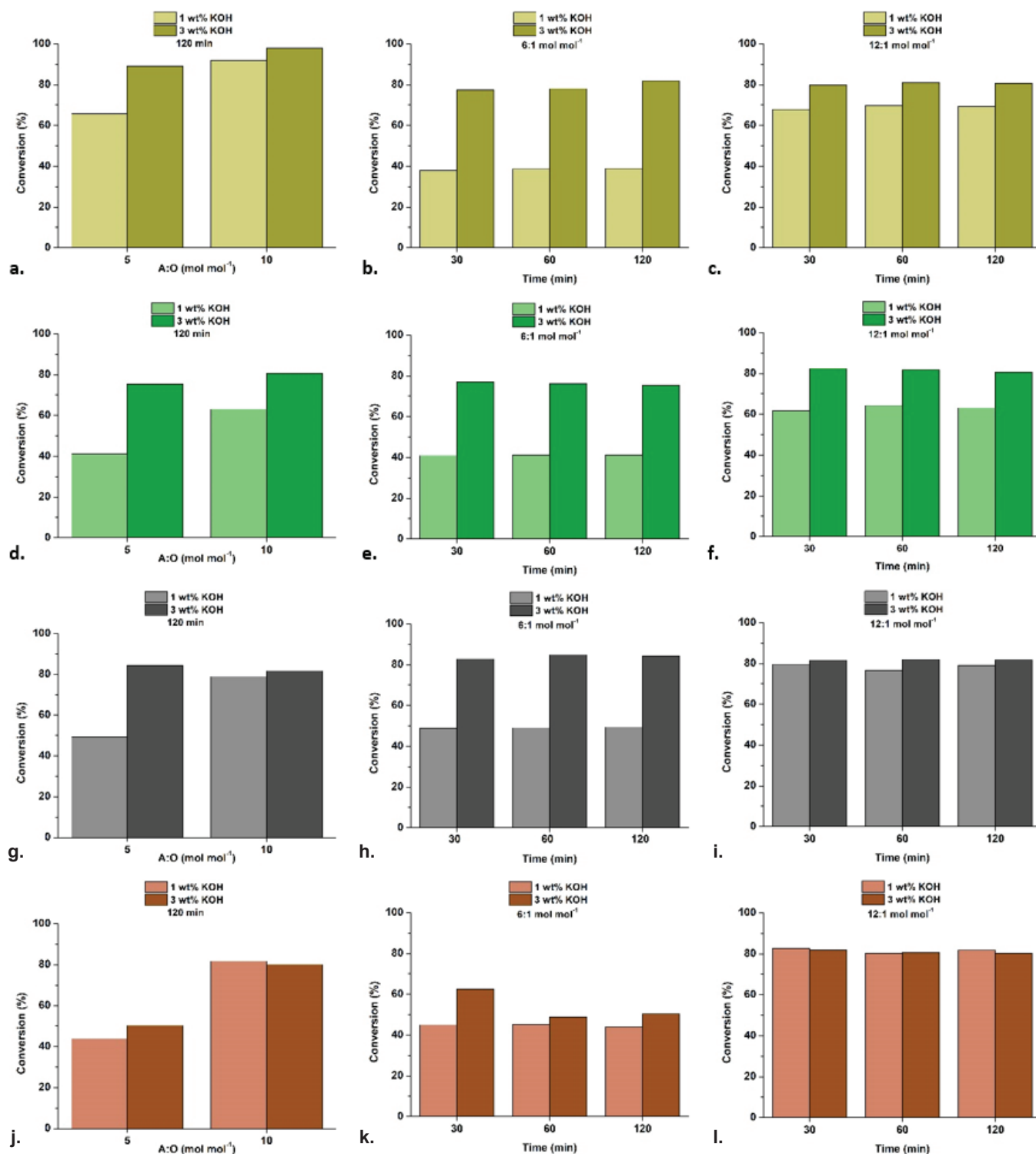


Fig. 6 – Dependence of the conversion of FAIPE from sunflower oil (1st row), rapeseed oil (2nd row), coconut oil (3rd row), and animal fat (4th row) on the mass fraction of KOH and: isopentanol to oil ratio after 120 minutes (1st column); time with the reactant ratio of 6:1 mol mol⁻¹ (2nd column); time with the reactant ratio of 12:1 mol mol⁻¹ (3rd column)

ranged from 80.8 to 83.8 %, whereas here they were slightly higher, ranging from 88.0 to 89.9 %. Furthermore, transesterification of waste cooking oil with 1-pentanol resulted in the highest conversions among all reaction systems, keeping the same parameter trends. Hence, it may be concluded that the amount of water or free fatty acids present in waste

cooking oil had no significant negative influence on the conversion of these reactions. In terms of FAIPE synthesis, all the reaction conversions of FAIPE were lower than were those of FAIBE from WCO, except those obtained at the lowest reactant molar ratio and the lowest catalyst mass fraction. In addition, the expected increase in reaction conversions

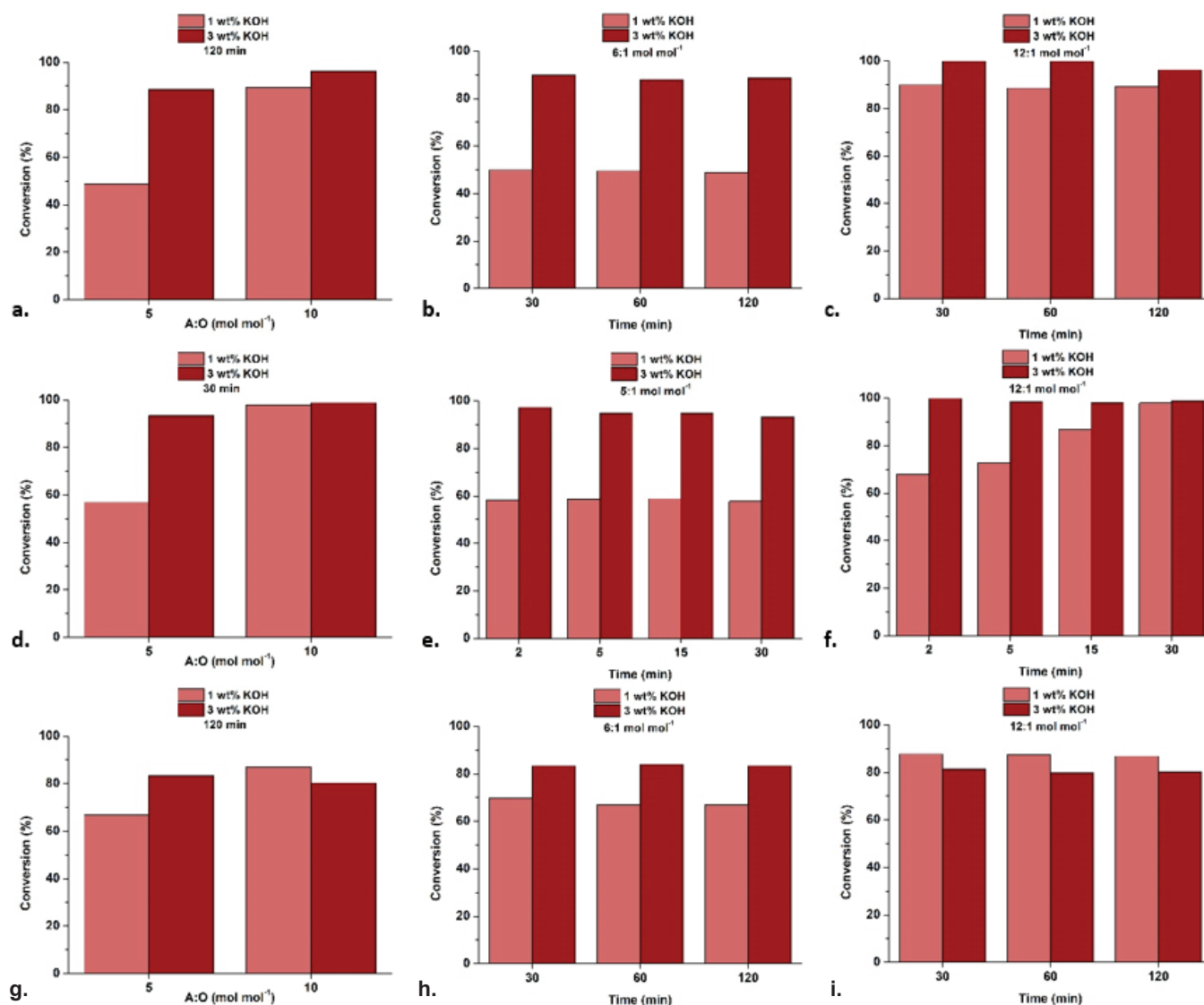


Fig. 7 – Dependence of the conversion of FAIBE (1st row), FAPE (2nd row), and FAIPE (3rd row) from waste cooking oil on the mass fraction of KOH and: alcohol to oil ratio after 120 minutes (1st and 3rd column) or after 30 minutes (2nd column); time with the reactant ratio of 5:1 mol mol⁻¹ (e) or 6:1 mol mol⁻¹ (b, h) (2nd column); time with the reactant ratio of 12:1 mol mol⁻¹ (3rd column)

with the increase in KOH mass fraction at the higher level of reactant molar ratio of 12:1 was not observed. Instead of increasing, these conversion values tended to decrease by 6.3–7.6 %. Time, however, continued to have little to no significance in this reaction system, as well, fluctuating within the range of up to 2.9 %.

The highest FAIBE conversion obtained when using waste cooking oil was 100.0 %, after 30 minutes, at the molar ratio of 12:1, and catalyst mass fraction of 3 %. With 1-pentanol, the highest conversion of 100 % occurred after only 2 minutes, at reactant molar ratio of 12:1, and catalyst mass fraction of 3 wt%. The highest conversion of fatty acid isopentyl esters of 87.7 % obtained using the same feedstock occurred after 30 minutes, at reactant molar ratio of 12:1, and catalyst mass fraction of 1 %.

Comparative result analysis

Fatty acid propyl, butyl, isobutyl, pentyl, and isopentyl esters were synthesized from various feedstock (sunflower oil, rapeseed oil, coconut oil, animal fat and waste cooking oil), via transesterification reaction in the presence of a potassium hydroxide catalyst.

After 30 minutes of the reaction, at temperature of 60 °C, and KOH mass fraction of 1 wt.% (Fig. 8), the increase in reactant molar ratio from lower (5:1 or 6:1) to higher (10:1 or 12:1) values resulted in the following changes in conversion of fatty acid propyl esters: from sunflower oil (76.1–91.6 %), from rapeseed oil (55.9–87.0 %), from coconut oil (79.6–99.1 %), and from animal fat (64.3–74.5 %). In the case of fatty acid butyl esters, these changes were as follows: for sunflower oil (74.6–99.3 %),

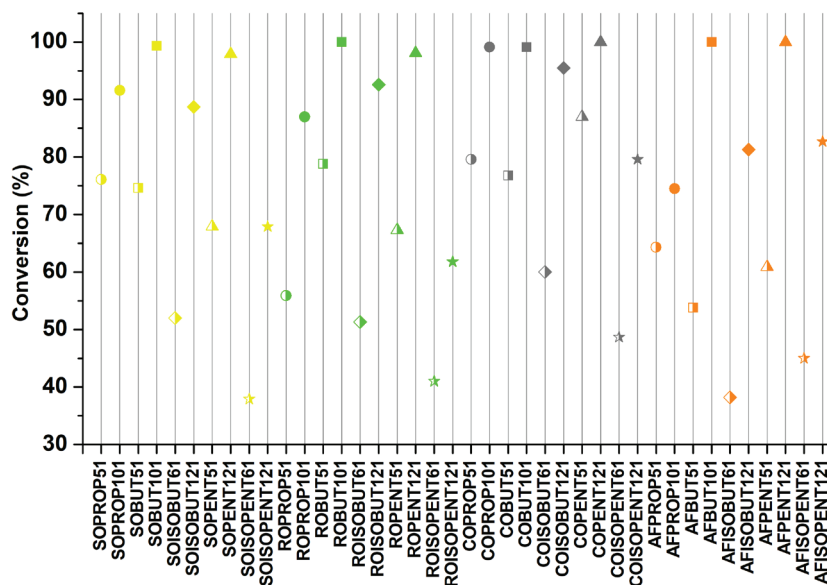


Fig. 8 – Conversions of biodiesels from sunflower oil (yellow), rapeseed oil (green), coconut oil (gray) or animal fat (orange), and propanol (circle), butanol (square), isobutanol (rhombus), pentanol (triangle) or isopentanol (star), in the presence of 1 wt.% KOH

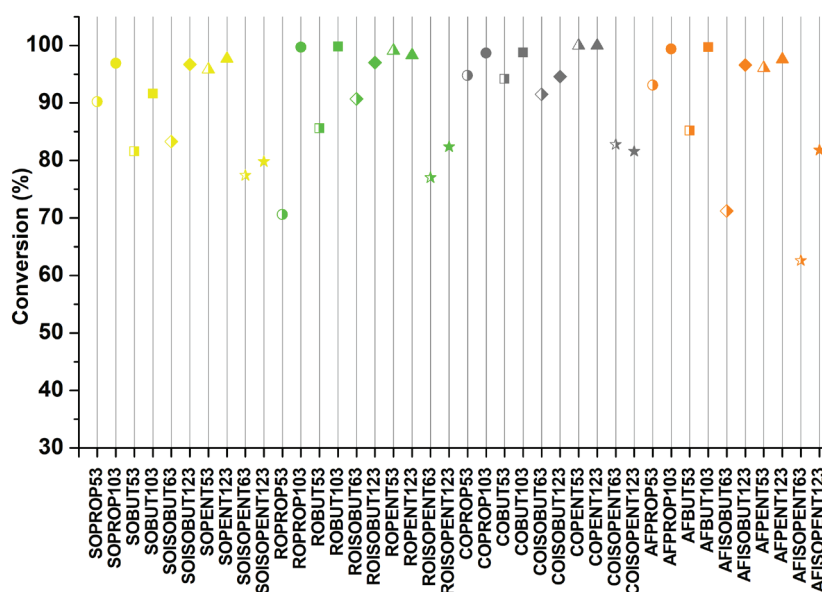


Fig. 9 – Conversions of biodiesels from sunflower oil (yellow), rapeseed oil (green), coconut oil (gray) or animal fat (orange), and propanol (circle), butanol (square), isobutanol (rhombus), pentanol (triangle) or isopentanol (star), in the presence of 3 wt.% KOH

for rapeseed oil (78.8–100.0 %), for coconut oil (76.8–99.1 %), and for animal fat (53.8–100.0 %). In the synthesis of fatty acid isobutyl esters, conversion change were as follows: for sunflower oil (52.0–88.7 %), for rapeseed oil (51.3–92.6 %), for coconut oil (60.0–95.5 %), and for animal fat (38.2–81.3 %). With fatty acid pentyl esters, the increase in the reactant molar ratio from 5:1 to 12:1 resulted in the conversion changes as follows: for sunflower oil (67.9–97.9 %), for rapeseed oil (67.3–98.1 %),

for coconut oil (87.0–100.0 %), and for animal fat (60.9–100.0 %). Finally, for fatty acid isopentyl esters, the increase in the molar ratio from 6:1 to 12:1 resulted in conversion changes as follows: for sunflower oil (37.9–67.9 %), for rapeseed oil (41.0–61.8 %), for coconut oil (48.7–79.6 %), and for animal fat (45.0–82.7 %).

After 30 minutes of the reaction, at temperature of 60 °C, and KOH mass fraction of 3 wt.% (Fig. 9), the increase in the reactant molar ratio from

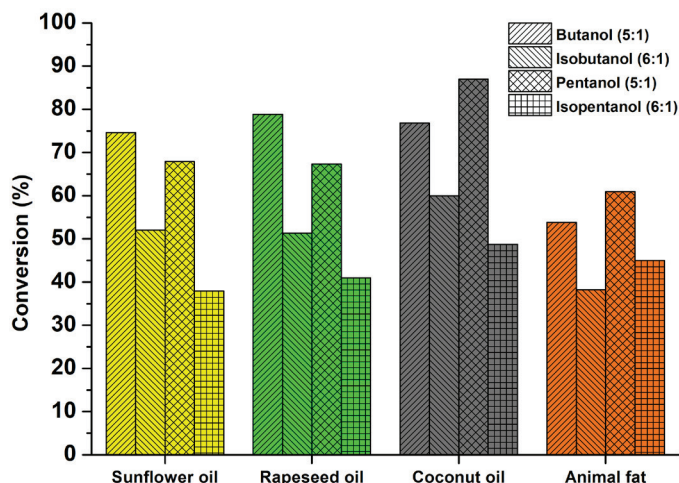


Fig. 10 – Dependence of the biodiesel conversions on the used source of triglycerides (sunflower oil (yellow), rapeseed oil (green), coconut oil (gray) or animal fat (orange)), at the lower catalyst amounts and alcohol/oil ratios

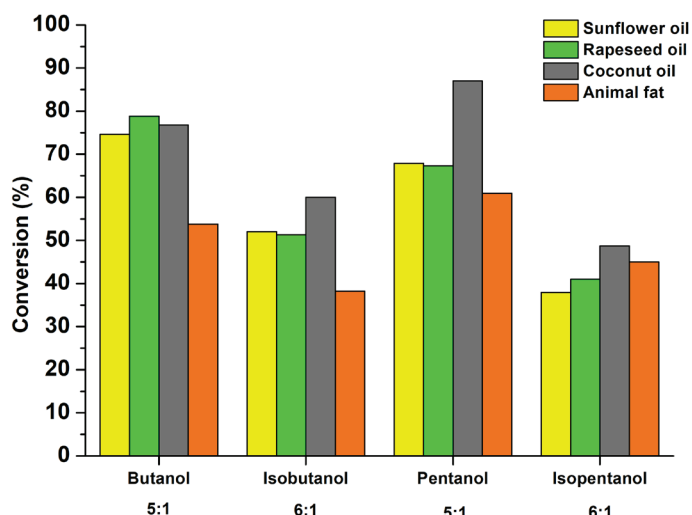


Fig. 11 – Dependence of the biodiesel conversions on the used alcohol (butanol, isobutanol, pentanol, or isopentanol)

lower (5:1 or 6:1) to higher (10:1 or 12:1) values resulted in the following changes in the conversion of fatty acid propyl esters: from sunflower oil (90.2–96.9 %), from rapeseed oil (70.6–99.7 %), from coconut oil (94.8–98.7 %), and from animal fat (93.1–99.4 %). In the case of fatty acid butyl esters, these changes were as follows: for sunflower oil (81.6–91.6 %), for rapeseed oil (85.6–99.8 %), for coconut oil (94.2–98.8 %), and for animal fat (85.2–99.7 %). In the synthesis of fatty acid isobutyl esters, conversion changes were as follows: for sunflower oil (83.3–96.7 %), for rapeseed oil (90.7–97.0 %), for coconut oil (91.5–94.6 %), and for animal fat (71.2–96.6 %). With fatty acid pentyl esters, the increase in the reactant molar ratio from 5:1 to 12:1 resulted in the conversion changes, as follows: for sunflower oil (95.8–97.7 %), for rape-

seed oil (99.1–98.3 %), for coconut oil (100.0–100.0 %), and for animal fat (96.1–97.6 %). Finally, for fatty acid isopentyl esters, the increase in the molar ratio from 6:1 to 12:1 resulted in the conversion changes, as follows: for sunflower oil (77.4–79.8 %), for rapeseed oil (77.0–82.4 %), for coconut oil (82.8–81.6 %), and for animal fat (62.6–81.8 %).

In general, the increase in the reactant molar ratio led to an increase in the reaction conversions, which was caused by the reversibility of the transesterification reaction, meaning that the addition of alcohol in a higher excess, moved the reaction equilibrium towards the reaction products.

To compare the effect of triglyceride type or alcohol used on conversion, the results were compared at the lowest catalyst amounts and alcohol/oil ratios (Fig. 10), due to their pronounced differences in conversion values.

Almost in all cases, the highest overall conversions were obtained in the systems with coconut oil (in the case of butanol, conversion value with rapeseed oil was 2.0 % higher compared to coconut oil), while the conversions in the systems with animal fat were dispersed towards the lowest conversions overall. This indicates that the feedstock with the shortest fatty acid chains in a triglyceride structure (lowest molecular weight), i.e., coconut oil, was converted to fatty acid alkyl esters the most, while increasing the molecular weight and degree of unsaturation led to an overall decrease in reaction conversions.

From the alcohol point of view (Fig. 11), we can compare the influence of alkyl chain length and branching of the alcohol on the conversion of biodiesels, again at the lowest catalyst amounts and alcohol/oil ratios.

For straight-chain alcohols, the results were ambiguous and no conclusion could be drawn, but for branched alcohols, an increase in alkyl chain length had a negative effect on the transesterification reaction almost in all cases. Comparing the influence of straight-chain and branched alcohols on the conversion, the use of the former led to higher conversions. This was due to the increased steric hindrance between the reactant molecules, which reduces the rate of the chemical reactions as well as the number of successful molecular collisions. Moreover, transesterification is a three-step reaction that begins with a nucleophilic attack of an alkoxide anion on one of the functional carbonyl groups in the structure of triglycerides. The affinity of the alkoxide anion for this group decreased as the polarity of the anion decreased, which was due to the increasing length of the alkyl chain, and resulted in lower conversion to the final product of the reaction – fatty acid alkyl esters.

Performed experiments with waste cooking oil showed similar results to those with sunflower oil, indicating that there was no significant negative influence of the amount of water or free fatty acids present in waste cooking oil on the conversion of these reactions.

Conclusions

The synthesis of fatty acid propyl, butyl, isobutyl, pentyl, and isopentyl esters is significantly influenced by the molar ratio of selected alcohol to oil, followed by the influence of the catalyst mass fraction. When using edible feedstock, the increase in these two parameters led to an increase in the reaction conversion. Feedstock with lower molecular weight (coconut oil) exhibited higher conversions to biodiesel, whereas an increase in the mo-

lecular weight and a decrease in the degree of saturation led to a decrease in the reaction conversion (animal fat). The transesterification of triglycerides with straight-chain alcohols led to higher conversion than the one with branched alcohols. The use of branched alcohol with higher molecular weight resulted in lower biodiesel conversions. As the conversion results for both waste and edible feedstock (sunflower oil) were similar, meaning that the amounts of water and free fatty acids present in the waste cooking oil were negligible in order to affect the reaction conversion, future experiments could be performed exclusively using waste feedstock. Furthermore, future research may involve further analysis of the obtained esters and their application properties, e.g., content of impurities after purification (diglycerides, monoglycerides, glycerol), density, viscosity, and others.

Supplement

Table S1 – Calculated conversion values for the synthesis of different fatty acid alkyl esters from sunflower oil

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion after 30 min (%)	Conversion after 60 min (%)	Conversion after 120 min (%)	
Sunflower oil	1-Propanol		5	1	76.1	66.4	65.7	
			5	3	90.2	88.9	89.1	
			10	1	91.6	98.1	92.0	
			10	3	96.9	97.8	98.0	
	1-Butanol			5	1	74.6	67.1	67.3
				5	3	81.6	84.7	89.4
				10	1	99.3	98.3	98.9
				10	3	91.6	99.1	100.0
	Isobutanol		30	6	1	52.0	47.2	50.1
				6	3	83.3	80.8	83.8
				12	1	88.7	88.5	88.4
				12	3	96.7	97.3	96.9
Isopentanol		60	6	1	37.9	38.6	38.9	
			6	3	77.4	78.0	81.7	
			12	1	67.9	69.7	69.4	
			12	3	79.8	81.1	80.5	
		120						

Table S2 – Calculated conversion values for the synthesis of different fatty acid alkyl esters from rapeseed oil

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion after 30 min (%)	Conversion after 60 min (%)	Conversion after 120 min (%)
Rapeseed oil	1-Propanol	30	5	1	55.9	65.2	68.1
			5	3	70.6	77.2	72.5
			10	1	87.0	84.2	88.9
			10	3	99.7	100.0	98.6
			5	1	78.8	76.8	74.6
			5	3	85.6	86.8	81.0
	1-Butanol	30	10	1	100.0	93.3	91.7
			10	3	99.8	98.9	99.9
			6	1	51.3	53.4	52.8
			6	3	90.7	90.6	92.1
			12	1	92.6	91.3	95.1
			12	3	97.0	96.0	96.9
	Isobutanol	120	6	1	41.0	41.1	41.1
			6	3	77.0	76.2	75.4
			12	1	61.8	64.3	63.1
			12	3	82.4	81.7	80.6

Table S3 – Calculated conversion values for the synthesis of different fatty acid alkyl esters from coconut oil

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion after 30 min (%)	Conversion after 60 min (%)	Conversion after 120 min (%)
Coconut oil	1-Propanol	30	5	1	79.6	84.6	83.2
			5	3	94.8	98.5	100.0
			10	1	99.1	100.0	98.0
			10	3	98.7	99.5	98.9
			5	1	76.8	89.9	95.0
			5	3	94.2	98.7	98.8
	1-Butanol	30	10	1	99.1	100.0	99.5
			10	3	98.8	99.0	100.0
			6	1	60.0	60.1	62.6
			6	3	91.5	91.0	91.0
			12	1	95.5	94.7	94.5
			12	3	94.6	97.7	96.7
	Isobutanol	120	6	1	48.7	49.0	49.4
			6	3	82.8	84.9	84.3
			12	1	79.6	76.6	78.9
			12	3	81.6	82.0	81.7

Table S4 – Calculated conversion values for the synthesis of different fatty acid alkyl esters from animal fat

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion after 30 min (%)	Conversion after 60 min (%)	Conversion after 120 min (%)
Animal fat	1-Propanol	30	5	1	64.3	61.0	61.8
			5	3	93.1	94.7	90.3
			10	1	74.5	80.3	87.3
			10	3	99.4	100.0	100.0
			5	1	53.8	56.6	58.0
			5	3	85.2	87.8	90.3
	1-Butanol	60	10	1	100.0	100.0	100.0
			10	3	99.7	98.8	100.0
			6	1	38.2	38.3	38.1
			6	3	71.2	70.8	70.9
			12	1	81.3	80.8	81.5
			12	3	96.6	96.9	96.2
	Isobutanol	120	6	1	45.0	45.3	43.9
			6	3	62.6	48.8	50.3
			12	1	82.7	80.1	81.7
Isopentanol		12	3	81.8	80.6	80.1	

Table S5 – Calculated conversion values for the synthesis of different fatty acid alkyl esters from waste cooking oil

Oil/Fat	Alcohol	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion after 30 min (%)	Conversion after 60 min (%)	Conversion after 120 min (%)
Waste cooking oil	Isobutanol	30	6	1	49.9	49.5	48.8
			6	3	89.9	88.0	88.6
			12	1	89.9	88.6	89.4
	Isopentanol	60	12	3	100.0	100.0	96.3
			6	1	69.8	67.0	66.9
			6	3	83.3	84.0	83.3
		120	12	1	87.7	87.4	86.9
			12	3	81.4	79.8	80.3

Table S6 – Calculated conversion values for the synthesis of fatty acid pentyl esters from different feedstock

Alcohol	Oil/Fat	Time (min)	Molar ratio A/O (mol mol ⁻¹)	Mass fraction of KOH (%)	Conversion (%) after (min):						
					2	5	15	30	60		
1-Pentanol	Sunflower Oil		5	1	68.3	67.8	68.8	67.9	68.9		
			5	3	90.9	90.6	91.3	95.8	96.3		
			12	1	100.0	99.2	99.9	97.9	97.0		
			12	3	98.5	98.6	97.7	97.7	97.8		
	Rapeseed Oil			5	1	68.5	70.4	72.4	67.3	/	
				5	3	97.4	97.6	97.5	99.1	/	
				12	1	99.6	99.6	99.7	98.1	/	
				12	3	98.0	97.6	97.5	98.3	/	
	Coconut Oil		2	12	3	98.0	97.6	97.5	98.3	/	
			5	5	1	82.9	86.2	85.5	87.0	/	
			15	5	3	100.0	98.8	100.0	100.0	/	
			30	12	1	100.0	100.0	100.0	100.0	/	
60			12	3	100.0	100.0	100.0	100.0	/		
120			5	1	61.2	60.8	61.1	60.92	/		
Animal Fat					5	3	95.9	95.4	97.0	96.14	/
					12	1	98.8	98.1	95.8	100.0	/
	12	3			98.3	98.1	98.2	97.6	/		
Waste Cooking Oil			5	1	58.2	58.6	58.8	57.0	57.7		
			5	3	97.1	94.9	94.8	93.3	94.0		
			12	1	67.8	72.7	86.8	97.9	97.6		
			12	3	100.0	98.4	98.1	98.8	97.4		

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