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The preparation of methyl esters and their application in epoxidation

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References

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Abstract

The doctoral thesis explores the preparation of methyl esters from vegetable oils and their use in epoxidation. Initially, methyl esters were synthesized via homogeneous (KOH) and heterogeneous (MgAl mixed oxides) transesterification. The study examined yield loss in homogeneous reactions and the impact of residual sodium compounds on the properties of mixed oxides and ester yields in heterogeneous reactions. In the second part, methyl esters were applied in epoxidation, with product composition analysis through various methods. The effects of reaction conditions on product properties were assessed, resulting in predictive equations for epoxide characteristics. Thermodynamic parameters (ΔH, ΔG) were calculated using quantum chemistry. Finally, novel titanium phosphate based heterogeneous catalysts enabled successful epoxidation of waste-derived methyl esters with successful scale-up.

Keywords

Vegetable oils, methyl esters, transesterification, epoxidation, mixed oxides, glycerol

Abstrakt

Disertační práce se zabývá přípravou methylesterů z rostlinných olejů a jejich využitím při epoxidaci. Nejprve byly methylestery syntetizovány pomocí homogenní (KOH) a heterogenní (MgAl smíšené oxidy) transesterifikace. V práci byly zkoumány ztráty výtěžku při homogenní reakci a vliv zbytkových sodných sloučenin na vlastnosti směsných oxidů a výtěžky esterů při heterogenní reakci. Ve druhé části práce byly methylestery využity k epoxidaci, kdy složení produktů bylo analyzováno různými metodami. Byl zkoumán vliv reakčních podmínek na vlastnosti produktů, což vedlo k vytvoření rovnic umožňujících předpověď vlastností epoxidů. Termodynamické parametry (ΔH, ΔG) byly získány kvantově-chemickými výpočty. Nakonec byly úspěšně použity nové heterogenní katalyzátory na bázi titánu a fosforu pro epoxidaci methylesterů z odpadních tuků a olejů včetně úspěšného převodu reakce do většího měřítka (scale-up).

Klíčová slova

Rostlinné oleje, metyl estery, transesterifikace, epoxidace, směsné oxidy, glycerol

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Introduction

Since the discovery of fire, humankind has been using biomass combustion for energy production. At the present time, modern technologies and the development of the standard of living is associated with an increasing energy consumption. Approximately 80.3 % of the energy consumed worldwide in 2023 came from non-renewable sources (such as coal, oil, natural gas, uranium) [1]. The declining reserves of fossil fuels and the effort of independency on foreign countries have lead to greater emphasis on the implementation of renewable sources for energy gain. The broad spectrum of renewable sources includes solar, geothermal, wind, hydro, or biomass energy [2].

The most commonly used biomass processing methods include: (i) fermentation of sugars [3] (production of bioethanol and biogas), (ii) pyrolysis of biomass (production of pyrolysis oil, synthesis gas) [4], (iii) hydrolysis of cellulose (production of sugars and bioethanol), and (iv) transesterification of oils (production of biodiesel) [5]. Bioethanol has a variety of applications, such as solvent, disinfectant, food preservative, and it is used for synthesis of propene [6], 1-butanol, hexanol [7], etc. Furthermore, bioethanol and biodiesel are used as additives to fuel for combustion engines. Biofuels are further classified into first, second, and third generation biofuels, according to the origin of the biomass from which they are produced.

First generation biofuels are derived from edible products, such as sugars, starches, fats and oils [8]. Brazil and the USA are among the largest producers of bioethanol as a first-generation biofuel [9]. Ethanol is usually added to gasoline at a 10 wt.% concentration and the resulting blend is labeled as an E10 mixture. The addition of ethanol results in an increased octane number, reduced CO_2 emissions, and sometimes lowers the price of gas. On the contrary, ethanol is hygroscopic (it absorbs water from air), which results in engine rusting; and lowers the calorific value of blend, resulting in an increased fuel consumption [10]. The biggest issue with first generation biofuels is their availability, cost, growth of monocultures, and competition with the food industry [11]. Second generation biofuels are synthesized from resources other than food crops, e.g., energy crops, forest residues (wood chips, leaves), grass, waste oils or other sources [12]. Therefore, the second generation biofuels do not influence the price of food. Cellulose, hemicellulose and lignin (contained in the biomass) need to be separated first, and can be then used for ethanol production [13]. Third generation biofuels are made from algae biomass. The algae needs less nutrients, pesticides, land area and water than conventional crops to produce the same amount of energy [14]. Furthermore, it contains 20-30 times more oil [15]. The major disadvantages of algae biomass are: (i) the need for controlled circulation of water of a certain purity, (ii) higher price of biodiesel, and (iii) the need for employement of staged reactor arrangement [16]. Furthermore, the high content of unsaturated fatty acids in the oil from microalgae disallows its application as additives for internal combustion engines without additional treatment.

Aims of doctoral thesis

- Study the loss of esters yield of various vegetable oils and their mixtures due to their leaching to glycerol phase based on used alcohol for the reaction and on the type of quenching of transesterification

- Synthesize MgAl mixed oxides with different amounts of residue sodium compounds and describe their effect on catalyst properties and ester yield of transesterification

- Study the epoxidation process of methyl esters from various vegetable oils and find suitable methods to analyze reaction products

- Study the epoxidation process of methyl esters from *Camelina sativa* and describe the influence of reaction conditions on the composition of products

- Study the influence of reaction conditions on the properties of epoxides from linseed and rapeseed methyl esters, and try to prevent the formation of unwanted subsequent products

- Compare performance of novel heterogeneous titanium phosphate based catalysts in the epoxidation process of methyl esters from waste cooking oils with other conventionally used catalysts for epoxidation

1 Biodiesel

Biodiesel is a biodegradable, non-toxic alternative fuel, usually synthesized from vegetable oils, grease, waste cooking oil, or animal fats. It is sometimes referred to as FAME, which stands for the mixture of Fatty Acid Methyl Esters. It is used as an additive to fuel in diesel engines [17]. Biodiesel is mainly produced through transesterification, a reaction between vegetable oils and a low-molecular alhocol.

1.1 Advantages and disadvantages

The main advantage of biodiesel application as a fuel is that it has zero overall carbon balance (all the CO_2 that is formed in combustion process had been absorbed by plants during photosynthesis) [18]. Another advantage is its lower emission of hydrocarbons, sulphur oxides and particulate matter compared to fossil diesel [19]; and it improves lubricating properties of fuel [20]. Finally, biodiesel is biodegradable and non-toxic; therefore, handling it is much safer [21].

The disadvantages of biodiesel compared to fossil diesel include: (i) lower calorific value than diesel, resulting in higher fuel consumption and lower performance of engine [22], (ii) lower cloud and pour point (temperature at which crystals start to appear and can clog up filters) [23], and (iii) higher NO_x emissions [24]. Furthermore, long time storage of biodiesel can lead to hydrolysis of methyl esters to free fatty acids [25]. Another issue is the competition of food vs. biofuel crops (especially in first-generation biofuels).

1.2 Feedstock for biodiesel production

Biodiesel can be synthesized from edible and non-edible vegetable oils, waste oils or animal fats. Each biodiesel has unique composition, which depends on fatty acids (FA) profile of used feedstock [26]. Feedstocks high in saturated FA content tend to solidify at a room temperature, whereas feedstocks high in unsaturated FA are not suitable for direct combustion in engines without additional treatment.

The production of biodiesel consists of two steps – (i) extraction of oils from plants and its processing, and (ii) conversion of oils/fats through various means. Transesterification is the most used method of conversion - it offers relatively high yield of biodiesel (>95 %), glycerol as a side product, requires mild reaction conditions (in homogeneous catalysis), and it is the most economically viable method [27].

2 Transesterification

The production of biodiesel is mostly implemented in the industry through transesterification reaction [28]. In the reaction, triacylglycerides (the main component of vegetable oils) react with a low molecular weight alcohol (usually methanol) in the presence of a catalyst (enzymatic, acidic or basic) [29], Fig. 1. Two main products of the reaction are (i) mixture of FAME, and (ii) glycerol. Glycerol is used in food processing, pharmacy [30], or as a precursor for synthesis of other chemicals (such as epichlorhydrin, or butanediol) [31]. The FAME is used for the production of other chemicals, such as lubricants, carboxylic acids, or monomers for polymerization [32].

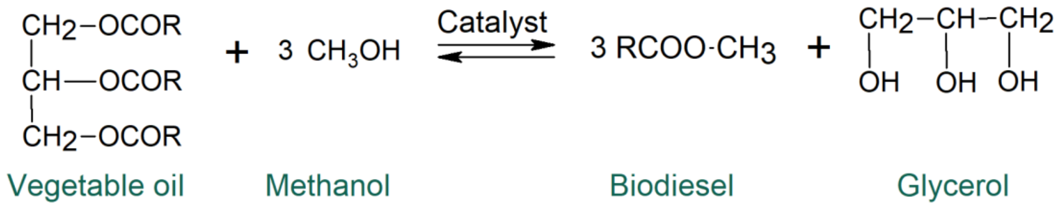

Fig. 1: *Transesterification scheme*

The products of transesterification are separated after the reaction according to their polarities. Glycerol phase (GP) contains mainly glycerol, salts, soaps, dissolved catalyst, water, alcohol, and trace amounts of esters and/or free fatty acids. Ester phase (EP) contains mainly esters, unreacted triacylglycerides and intermediate products, trace amounts of water and glycerol [33]. The quantity and type of impurities produced in transterification depend on the specific reaction conditions, catalyst type, and feedstock [34]. Mutual contamination of phases is undesirable as it requires employment of purification processes and increases the cost of products.

2.1 Catalysis in transesterification

Transesterification is usually catalyzed by enzymes or acidic/basic chemicals [35]. Catalysts can be homogeneous (same phase as the reaction mixture, e.g., KOH, NaOH) or heterogeneous (different phase, e.g., mixed oxides, zeolites).

In homogeneous acid catalysis, strong mineral acids (H_2SO_4, HCl, or BF_3) are often used [36]. Their major advantage is the low sensitivity to water and FFA content in oil because saponification does not occur (a basic environment is needed). Major disadvantages include: (i) lower reaction rate than basic catalysts, (ii) corrosiveness of the environment, (iii) requirement of higher molar ratio of alcohol to oil (20:1 – 245:1), (iv) need for higher reaction temperatures (>100 °C), and (v) difficult separation from products [37]. However, the separation can be improved by the use of heterogenenous catalysts, such as $AlCl_3$, $ZnCl_2$, or SnO_2, zeolites, or heteropolyacids [38].

Homogeneous basic catalysts (hydroxides or methoxides of sodium and potassium) are mostly used in industry. Major advantages are: (i) high activity (i.e., quick reaction – usually 60-120 minutes), (ii) low catalyst cost, and (iii) mild reaction conditions (60 °C, atmospheric pressure). Disadvantages include: (i) sensitivity to FFA and water (soaps are formed - reduced yield) [39], (ii) use of vast amounts of washing water for purification of products, and (iii) the inability to reuse the catalyst [40]. The issues of catalyst recovery can be adressed by the use of heterogeneous catalysts, such as mixed oxides. However, disadvantage of heterogeneous basic catalysts is their lower catalytic activity (a higher reaction temperature is needed, often 60-150 °C to obtain similar yields of esters [41]. Furthermore, metals from catalysts can leach into the reaction mixture, leading to catalyst deactivation, problems with its structural stability, and contamination of products [42].

2.2 Purification of products of a homogeneous transesterification

Purity of glycerol is strongly influenced by reaction conditions of transesterification, such as type of alcohol used, and/or a method of reaction stopping [43]. The ester content in GP (ester losses) generally increases with an increasing amount of soaps. As a result, ester yield is reduced and the cost of glycerol is increased (purification is needed).

In Paper I, the transesterification of different vegetable oils and their mixtures was carried out using various alcohols (methanol, ethanol, or butanol) with KOH as a catalyst. Furthermore, the method of reaction stopping (catalyst neutralization by precise addition of phosphoric acid, saturation by CO_2, or saturation by CO_2 in water) was studied. The content of esters was determined using GC-FID.

The lowest ester loss was observed for methyl esters (ME, 6-8 wt.%). On the contrary, the highest loss of esters was observed for transesterification with ethanol (20-34 wt.%), and the loss of 16-30 wt.% was observed for butyl esters (BE) due to high soap formation. The saturation by CO_2 in water increased ester losses up to 40 wt.% due to dissociation of soaps.

Fatty acid profiles of butyl esters in both phases were similar independent of reaction stopping, whereas methyl esters of oleic acid (CO_2 stopping) and linolenic acid (H_3PO_4 stopping) had the highest affinity towards glycerol phase (Fig. 2). The losses of methyl esters varied from oil to oil, e.g., 2.9 and 3.5 wt.% for acidic and gaseous stopping of *Camelina sativa* oil, respectively; or 7.3 and 6.6 wt.% for acidic and gaseous stopping of rapeseed oil, respectively. In comparison, losses of BE of rapeseed oil were much higher (18.1 wt.% for H_3PO_4 stopping, and 16.4 wt.% for CO_2 stopping), which was caused by an increased formation of soaps. Eventually, high pH (>10, insufficient catalyst neutralization) of reaction mixture and higher ionic strength increased the content of linolenic acid esters in glycerol phase.

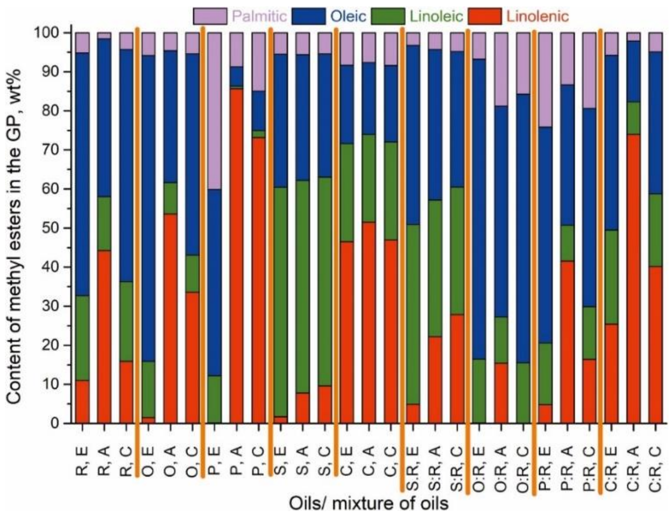

Fig. 2: *Fatty acids distribution profiles after methanolysis*

Note: In Fig. 2, R = Rapeseed oil; O = Olive oil; P = Palm oil; S = Sunflower oil; C = *Camelina sativa* oil; S:R, O:R, P:R and C:R = mixture of these oils; E = composition of ester phase after reaction; A = composition of glycerol phase after stopping with phosphoric acid; C = composition of glycerol phase after stopping with CO_2

2.3 Heterogeneous catalysis in transesterification

Various heterogeneous catalysts can be used for the synthesis of methyl esters, such as mixed oxides, or zeolites [44]. The mixed oxides, which had been synthesized from hydrotalcites, were further studied because of their low cost, easy preparation and high yield of methyl esters.

Hydrotalcites and mixed oxides

Hydrotalcites are materials derived from brucite mineral $Mg(OH)_2$. They have alternating cation and anion layers (Fig. 3). The cation layers are made of hydroxides in octaedric crystal modification, in which various M^{2+} and M^{3+} ions of metals are embedded (such as Mg^{2+}, Ni^{2+}, Cu^{2+}, Ca^{2+}, Al^{3+}, Fe^{3+}, etc.). The anion layers are made of water and anions (such as CO_3^{2-}, Cl^-, OH^-, etc.) Hydrotalcites are widely used as building materials additives [45], adsorbers [46], or for CO_2 capture [47].

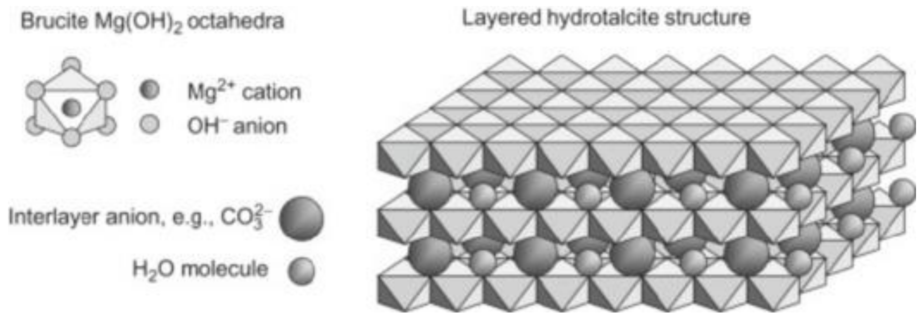

Fig. 3: *Hydrotalcite layered structure [48]*

Hydrotalcites can be synthesized via three routes: (i) sol-gel, (ii) hydrolysis of urea, or (iii) co-precipitation method with hydroxides or carbonates. Materials are usually washed after the synthesis, however, throughout the literature research, it was found that the procedure for washing the materials differs (various amounts of water are used, if any). Chemicals left in hydrotalcites and mixed oxides can influence properties of materials, which was the focus of Paper II. All hydrotalcites in this work were prepared by co-precipitation method with NaOH solution (molar ratio Mg:Al 3:1 based on literature research). The materials were washed several times with redistilled water and filtered, so they contained various amounts of residue sodium compounds (from NaOH).

Mixed oxides (MO) are materials synthesized from hydrotalcites by their temperature decomposition. In this process, the layers of hydrotalcites collapse and MOs are synthesized. During TGA-MS analysis, a decomposition of nitrates was detected by NOx signal at an interval 350-650 °C. At this interval, $NaNO_3$ decomposed to $NaNO_2$, which further decomposed to Na_2O, which will play a key role in transesterification. Mixed oxides are characterized by weak basic sites (OH^-), medium strength basic sites (Mg^{2+} - O^{2-}pairs) and strong basic sites (O^{2-}), which are all suitable for basic transesterification [49]. The MOs have high specific surface area (usually 100-300 m^2/g) [50], even distribution of basic centres [51], and temperature stability up to 800 °C.

The content of sodium ions in filtrate was determined by Na^+ ion selective electrode. The relative amount of sodium left in materials was calculated from the known amount of NaOH used in co-precipitation minus the amount of sodium determined in the filtrate.

Afterwards, XRD was used to confirm successful synthesis of materials. The analysis revealed signals typical for hydrotalcites and mixed oxides (the syntheses were successful). Furthermore, a signal at 29.4° was detected (red rectangle in Fig. 4), which was attributed to $NaNO_3$ signal. Sodium nitrate had been probably formed by the recombination of ions (hydroxide was exchanged for nitrate) during the synthesis of materials.

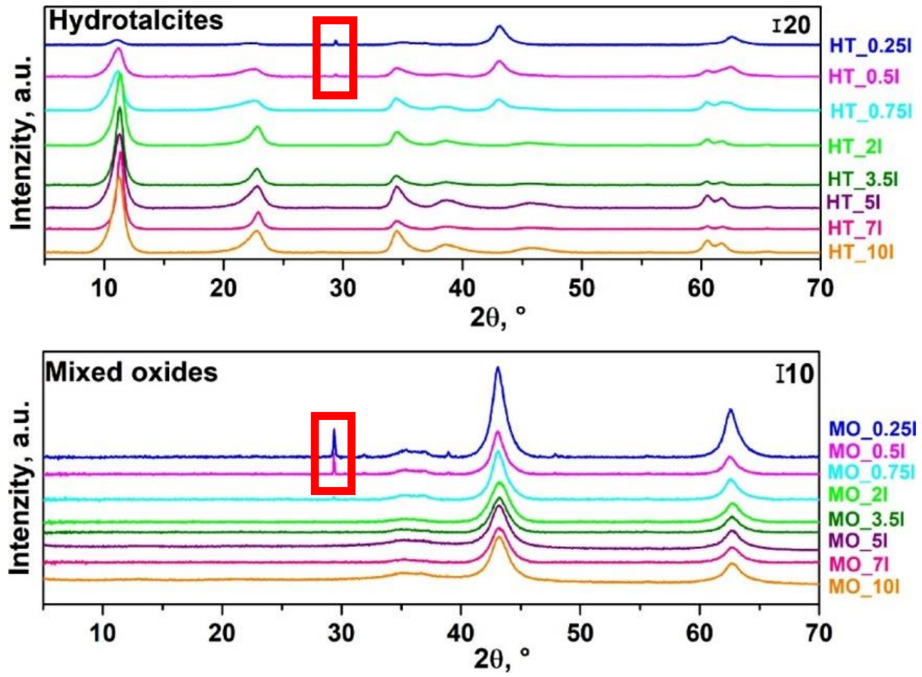

Fig.4: *XRD diffractograms of hydrotalcite and mixed oxides washed with various amounts of redistilled water*

TPD-CO_2 method was used to study the basicity of MOs. The amount of desorbed CO_2 increased with an increasing amount of washing water, i.e., decreasing amount of sodium compounds (Fig. 5B). Sodium compounds likely contributed to the blockage of MO pores, which decreased their overall basicity. Additionally, the less washed materials showed larger desorption signals at higher temperatures (300-450 °C, medium strong basic sites), whereas the more washed materials showed predominantly signal at lower temperatures (70-180 °C, weak basic sites). Furthermore, artificial addition of $NaNO_3$ decreased the amount of CO_2 desorbed, which higlights its influence on the properties of MOs.

Eventually, transesterification was carried out and the composition of ester phase was determined using GC-FID (Fig. 5C). Higher ester yields were obtained (63-66 wt.%) with the least washed catalysts. With the increasing amount of washing water, the yield decreased to only 19 wt.% for MO washed with 10 dm^3 of water. The Na_2O, which had formed during the calcination, probably leached into methanol. It then reacted with water in methanol to form NaOH, which acted as a homogeneous catalyst, increasing ester yield. Artificial addition of $NaNO_3$ increased ester yield of the most washed material (from 19 to 50 wt.%).

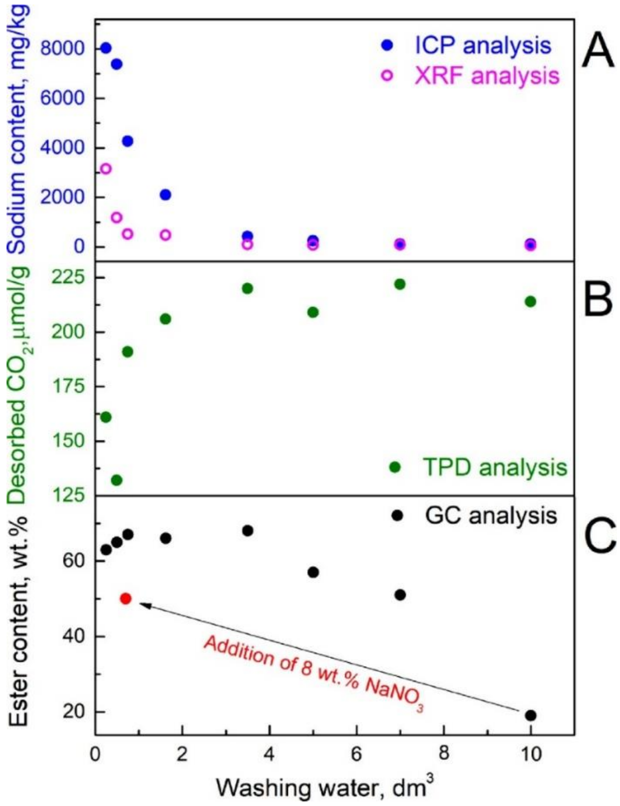

Fig. 5: *Dependency of: (A) results of chemical analysis, (B) TPD-CO_2, and (C) transesterification on the amount of washing water*

3 Epoxidation

Currently, the consumption of glycerol increases every year [52]. With the transition of combustion engines to electric and/or hydrogen engines, a new problem arises in the production of glycerol – excess of methyl esters. Moreover, MEs from second-generation renewables (e.g., *Camelina sativa*) may have unsuitable properties (e.g., high iodine value, viscosity) for use as diesel additives [53]. However, their high iodine value makes them suitable for epoxidation.

An epoxidation is a reaction of a double bond located between two adjacent carbon atoms and an oxygen atom. The oxygen atom is usually in form of a peroxyacid (performic or peracetic), or in a form of oxygen atom adsorbed on a heterogeneous catalyst [54]. A product of epoxidation is an epoxide bond, sometimes referred to as an oxirane bond, which is an oxygen atom bonded to two adjacent carbon atoms in a hydrocarbon chain. Epoxides are used as surface protective agents [55], additives to paints [56], or for CO_2 capture [57]. Additionally, they serve as precursors for synthesis of other chemicals, such as alcohols [58], or epoxy resins [59].

Epoxides from methyl esters of vegetable oils can be synthesized by two methods. The first methods is through *Prileschajew/Prilezhaev* route, where performic or peracetic acid is synthesized *in situ* from corresponding organic acid and H_2O_2 [60]. The per-acid then reacts with the double bond of a carbon chain and an epoxide bond is formed (Fig. 6). The disadvantage of this method is a formation of unwanted by-products (mainly alcohols) caused by the epoxide ring opening (sometimes referred to as oxirane bond cleavage) [61].

The second method of methyl esters epoxidation is with the use of heterogeneous catalysts. Main advantages of heterogeneous catalysts include their reusability and no need for formic or acetic acid. On the contrary, heterogeneous catalysts need higher reaction temperatures to obtain the same yield of epoxides and a co-solvent is needed (usually large amounts of acetonitrile are used).

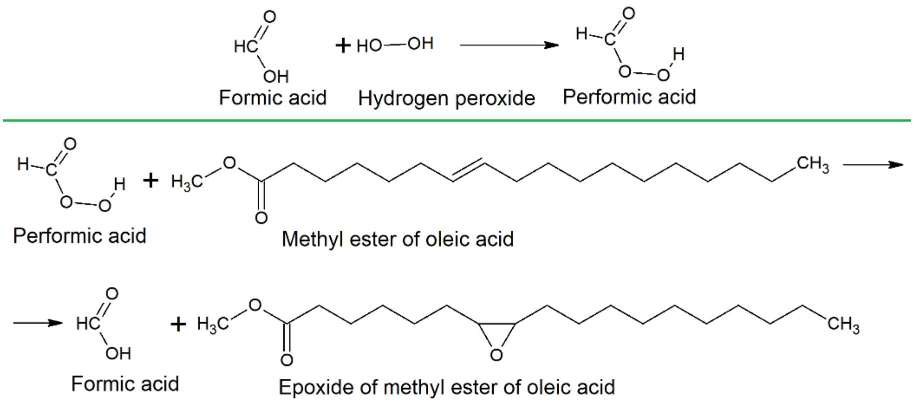

Fig. 6: *A reaction scheme of epoxidation of ME of oleic acid*

3.1 Analysis of reaction products

Identification of epoxidation products is challenging, as the number of possible epoxides rises exponentially with increasing double bonds in fatty acid MEs. Each double bond can exist in cis- or trans- form, and each epoxide may undergo oxirane bond cleavage. Most products lack analytical standards and mass spectral data.

Iodine value (*IV*, the amount of unreacted double bonds) and epoxy value/index (*EI*, the amount of epoxide bonds in a sample) determined by titration are widely used to monitor epoxidation [62]. However, these methods are insufficient for identification of individual reaction products, and they lack in accuracy due to visual determination of titration equilibrium. The aim of Paper III was to develop methods suitable for identification of individual epoxidation products, enabling better process control and reduced by-products formation.

A simulated distillation method was used first. A signal at 325 °C corresponded to ME of palmitic acid, and a signal at 360 °C was attributed to ME of C18 molecules (stearic, oleic, linoleic, and linolenic acid). After the epoxidation, two additional signals appeared at 375 and 395 °C, which were attributed to epoxides (extra oxygen atom increases the boiling point of ME).

Infrared spectroscopy with Attenuated Total Reflectance (IR-ATR) was used afterwards, Fig. 7. Several absorption bands, which allow to directly monitor the epoxidation process, were identified: (i) a broad band at 3100-3600 cm^{-1} was attributed to -OH groups (Fig. 7A), (ii) band at 3010-3012 cm^{-1} was attributed to =C<u>H</u>$_2$ bond (Fig. 7B), and (iii) band at 824-845 cm^{-1} was attributed to an epoxide bond (Fig. 7C). The broad band at 3100-3600 cm^{-1} was attributed to alcohol functional group of by-products because methyl esters of linseed oil have a high content of linolenic acid, which is more prone to oxirane bond cleavage [63].

Then, HPLC-RI was used. Methyl esters with an epoxide bond were eluted sooner (5.0-11.4 min) than pure methyl esters without epoxide bonds (11.5-25.0 min). Moreover, retention time increased with shorter carbon chains and fewer double bonds. However, this method was not sufficient to distinguish between intemediate and final products of the same molecule (such as in case of linolenic acid).

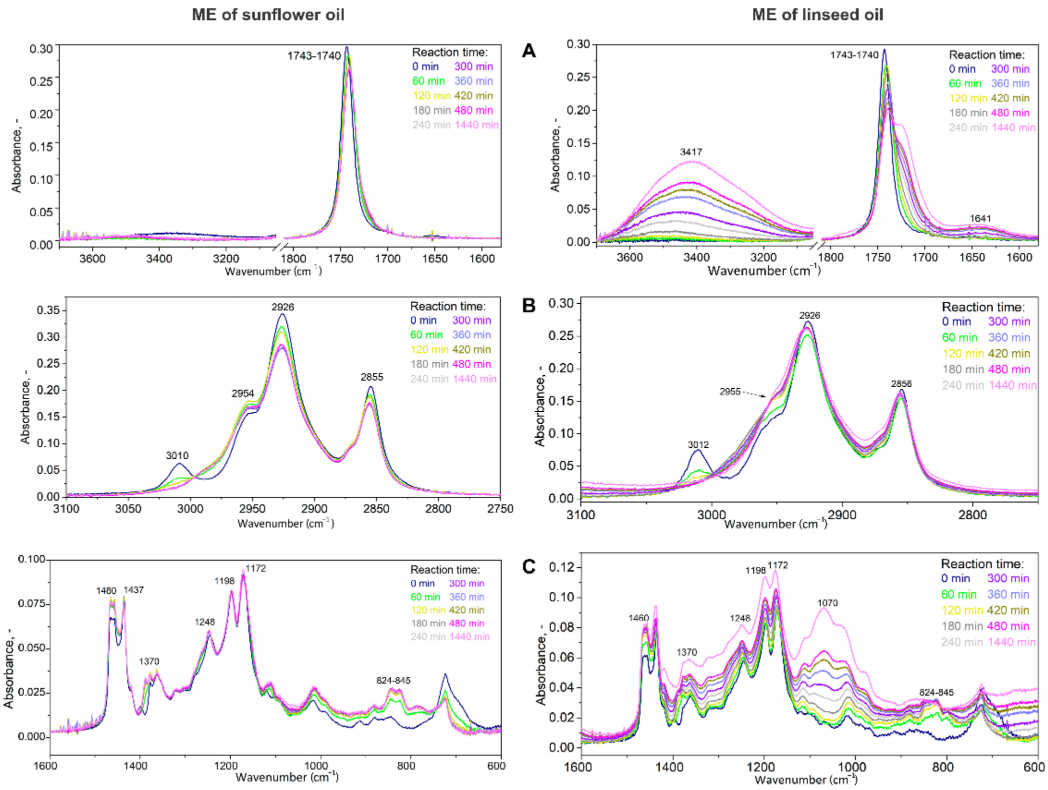

Fig. 7: *Infrared spectra of epoxides of various methyl esters*

Eventually, gas chromatography with mass spectrometer (GC-MS) was used (identification of retention peaks is presented in Fig. 8). Individual products were identified by mutual comparison of epoxides from various ME (rapeseed oil rich in C18:1, sunflower oil rich in C18:2, linseed oil rich in C18:3, and *Camelina sativa* rich in C20:1). Furthermore, C17:0 was used as an internal standard (this fatty acid does not naturally occur in plants) to improve the accuracy of determination.

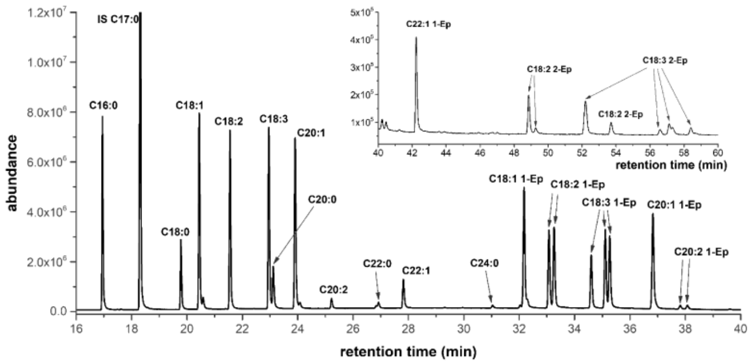

Fig. 8: *GC-MS chromatogram*

All methyl esters without any oxirane ring were successfully identified by comparison of their m/z spectra with the database. Other products were denoted based on the number of carbon atoms, the number of double bonds before epoxidation, number of epoxide bonds after the reaction, and roman number indicates some form of geometric conformation (cis-/trans- combinations). E.g., C18:3 2-Ep I is an epoxide of linolenic acid ME with two oxirane bonds and some geometric conformation (I). In conclusion, GC-MS is a suitable method for identification and quantification of products of epoxidation with high reproducibility, fast analysis, and low measurement cost.

Subsequently in Paper IV, epoxides were analyzed using Raman spetroscopy. A signal at 1659 cm^{-1} was attributed to C=C bond. A correlation of areas of this signal of methyl esters of different vegetable oils with various degrees of epoxidation with their respective iodine value was made (Fig. 9). A linear model in range of 0-80 g I_2/100 g was obtained. This correlation can be used to determine *IV* with the use of Raman spectroscopy, which: (i) is quick, (ii) can be carried out *in situ*, (iii) does not need chemicals (compared to classical titration), (iv) and is universal for all vegetable oils.

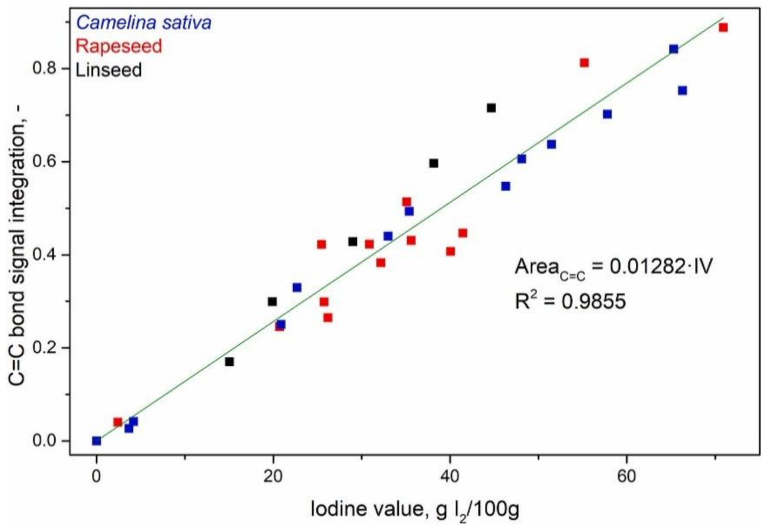

Fig. 9: *Correlation plot of C=C signal integration vs. Iodine value*

3.2 Optimization and description of homogeneous epoxidations

Epoxidation of *Camelina sativa*

As the shift toward sustainable methyl ester sources continues, second- and third-generation oils, such as waste cooking oils (WCO), are favored over first-generation ones. WCO is a renewable, low-cost feedstock, which was used in several papers [64, 65]. Although the application of WCO for epoxidation looks primising, it comes with several issues. First, WCO require pre-treatment, such as degumming, filtration, neutralization, deodorization, etc. More importantly, the composition (fatty acid profile) of WCO is strongly dependent on the type of used oil in cooking. Therefore, its iodine value is ambiguous, and the quality of products can vary. On the contrary, the *Camelina sativa* (second generation source) has always similar profile of fatty acids and, therefore, the quality of products is clearly defined.

Camelina sativa (CS) is a non-edible plant with short ripening time (90-110 days), cold tolerance, requires low amounts of water and fertilizer, and has relatively high *IV* (142-167 g I_2/100 g of oil), which is favorable for epoxidation [66]. The aim of Paper IV was to describe relationships between reaction conditions and properties of products in detail, and to possibly explain these relationships through thermodynamic calculations.

A Plackett-Burman experimental design was utilized to find relationships between 7 independent variables (reaction temperature T, reaction time t, molar ratio of H_2O_2 to double bonds MR_H, molar ratio of formic acid to double bonds MR_F, intensity of stirring ω, H_2SO_4 as a co-catalyst *cat*, and oil un/refinement *ref*) and 6 properties of epoxides – dependent variables (*IV*, *EI*, viscosity, density, yield of epoxides, and ME conversion).

High *IV* (100 – 124 g I_2/100 g) was obtained when short reaction time (1 h) was utilized, independent on other reaction conditions. On the contrary, low *IV* (<5 g I_2/100 g) was achieved when high reaction temperature (50 or 60 °C) with long reaction times (>3 h) was used. Furthermore, the highest *EI* (>3.2 mol/kg) was achieved when the reaction was carried out without H_2SO_4, which is often used in epoxidations with acetic acid.

Principal component analysis (PCA) was used to reveal hidden relationships between variables. Fig. 10A showed that the increasing t, T, and MR_F, decreased the concentration of ME from unsaturated fatty acids (double bonds reacted to epoxide bonds, which is favorable). On the contrary, the concentration of methyl esters from saturated fatty acids (C16:0, C18:0) did not change. However, their concentration decreased with an increasing amount of *cat*, because hydrolysis of methyl esters took place. Fig. 10B revealed that products and intermediate products form groups (i) – (v) depending on the total number of double bonds, and on the number of epoxide bonds. Groups (i) and (iii) were formed by fully epoxidized methyl esters, whereas groups (ii), (iv), and (v) were formed by intermediate products, whose concentration decreased with an increasing t and T. Fig. 10C revealed that higher T and longer t has the strongest influence on the decrease of iodine value (IV_D), and conversion of FAME (X_{ester}). Furthermore, higher MR_F, MR_H and *cat* are responsible for an increased viscosity and density of products, probably due to oxirane bond cleavage. Eventually, higher *EI* and yield of epoxides (Y_{epox}) is positively influenced by an increased *t*. Most importantly, in all PCA graphs, un/refinement of oil is not present. This means that oil refining is redundant, which can lower the price of products.

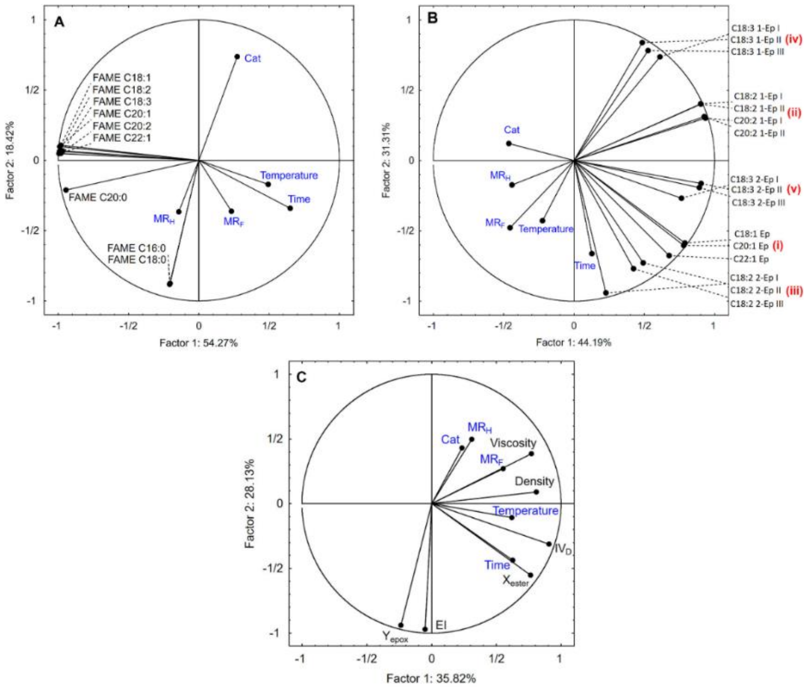

Fig. 10: *PCA results – Relationship between reaction conditions and (A) reactants, (B) products, (C) properties of epoxides*

Afterwards, thermodynamic calculations were carried out. First, calculated enthalpies of epoxidation were between −247 and −269 kJ/mol, which is in correlation with literature. Then, Gibbs‘ energies of epoxidation were calculated. Mono-unsaturated fatty acids (C18:1, C20:1, C22:1) showed similar Gibb’s energy (−257 to −260 kJ/mol) explaining their cohesion in group (i) in Fig. 10B. For poly-unsaturated acids (C18:2, C18:3), the first epoxidation step had Gibb’s energy of −257 to −260 kJ/mol, ragardless of double bond position – except for C_{12}-C_{13} bond with −250 kJ/mol and −248 kJ/mol Gibb’s energy in C18:2 and C18:3, respectively, likely by limited accessibility, as observed by Orellana-Coca C. et al [67]. While these calculations clarify epoxidation trends, they don't fully explain all groupings in Fig. 10B.

Optimization of rapeseed and linseed methyl esters epoxidation

Many by-products (mainly alcohols) are formed in homogeneous epoxidation. This phenomenon is caused by high reactivity of an epoxide ring, which undergoes oxirane bond cleavage in an acidic environment. These subsequent reactions can be minimized by the optimization of reaction conditions. However, vegetable oils have various profiles of fatty acids, which differ in reactivity; therefore, they need to be optimized separately. Several papers focused on optimization of epoxidation were published, however, many experiments (9-27) are needed to study the influence of reaction conditions on properties of products. The aim of Paper V was to minimize the number of required experiments using Plackett-Burman experimental design, and to create mathematical models that could predict properties of products before their synthesis.

First, a comparison of epoxidations of methyl esters with different fatty acid profiles was carried out under the same reaction conditions to investigate how the yields and properties of epoxides vary. Rapeseed and linseed methyl esters were further used for optimization of epoxidation due to: (i) high conversion of double bonds but low yield of rapeseed epoxides, (ii) low conversion of double bonds and low yield of linseed epoxides, and (iii) various profiles of fatty acids with very different *IV* (105.7 g I_2/100 g for rapeseed and 181.3 g I_2/100 g for linseed oil).

A principal component analysis was used to find relationships between 7 independent variables (reaction temperature T, reaction time t, molar ratio of H_2O_2 to double bonds MR_H, molar ratio of formic acid to double bonds MR_F, stirring ω, presence of H_2SO_4 co-catalyst *cat*, and initial iodine value IV_0) and 6 properties of epoxides – dependent variables (IV_D, *EI*, kinematic viscosity, density, *RCO*, and MEs conversion X_{ME}). Variable limits were set based on literature research, and 20 experiments were conducted, with some repeated several times to confirm reproducibility.

A series of equations (Eq 1 to Eq 6) were obtained using programme QC Expert 2.5. Statistical parameters such as residual square of sums, coefficient of determination, Atkinson distance, Williams parameter, and p-value were monitored to construct model equations. The standard deviation of the model is approximately ±5 rel.%. The equations revealed that higher IV_D can be achieved by: (i) an epoxidation of ME with higher initial iodine value (from linseed oil), because more double bonds increase the reaction rate, (ii) higher amounts of formic acid due to an increase in formation of performic acid, which is the rate-determining step in a homogeneous epoxidation [68], and (iii) longer t and higher T (the reaction is faster and can proceed more thoroughly).

$$IV_D = 66.90 + 3.89IV_0 + 11.32MR_F + 16.61T + 14.20t \quad \text{Eq (1)}$$
$$EI = 2.69 + 0.36IV_0 + 0.62MR_F + 0.78T + 0.83t \quad \text{Eq (2)}$$
$$RCO = 52.96 – 5.09IV_0 + 15.22MR_F + 17.43T + 16.41t \quad \text{Eq (3)}$$
$$X_{ME} = 77.13 + 8.01IV_0 + 16.03MR_F + 16.53T + 14.20t \quad \text{Eq (4)}$$
$$\text{kinematic viscosity} = 9.13 + 2.50IV_0 – 1.78MR_H + 2.07T + 2.94t \quad \text{Eq (5)}$$
$$\rho = 0.929 + 0.017IV_0 – 0.015MR_H + 0.016T + 0.021t \quad \text{Eq (6)}$$

To achieve higher *EI* and *RCO*, higher MR_F (performic acid formation is quicker), higher T and t (the reaction proceeds faster and more thoroughly) were needed. Moreover, *EI* was positively influenced by higher IV_0 (more double bonds can be epoxidized), whereas *RCO* was negatively influenced by higher IV_0. It is because ME with high *IV* contain more C18:2 and C18:3 fatty acids, which are epoxidized faster, and can therefore undergo oxirane cleavage reactions much sooner than MEs rich in oleic acid.

Higher viscosity, favorable for biolubricant epoxide applications, was obtained with higher IV_0, T and t (more epoxides were formed). Higher density, favorable for transportation of epoxides, was achieved with higher IV_0, T and t (more epoxides were formed), and lower MR_H (less oxirane bond cleavage took place). Most importantly, all parameters were independent on ω (sufficient to provide good contact between phases), and *cat* (not required). Moreover, MR_H concentration was optimized because it was not present in equations.

3.3 Heterogeneous catalysis in epoxidation

The issue of oxirane bond cleavage in homogeneous epoxidation can be diminished by the use of heterogeneous catalysts, as these systems do not include acids (formic/acetic) responsible for degradation of an epoxide bond [69]. Moreover, the catalyst can be easily removed and reused for epoxidation. On the contrary, a solvent is needed (usually acetonitrile, or tert-butanol) [70], because non-polar esters and polar aqueous solution of H_2O_2 are immiscible liquids. By minimizing the number of phases in the system, the interaction of reactants with active sites of the catalyst is increased [71].

Heterogeneous catalysts in epoxidation work by transferring the oxygen from hydrogen peroxide (or other oxidant) to a double bond via active sites. Therefore, a transition metal (such as W, V, Ti, Mo, etc.) needs to be present in a catalyst in an active oxidation form [72, 73]. Titanium silicate derived from zeolite (commercially known as TS-1) is the most often used catalyst for heterogeneous epoxidation of propene with H_2O_2 [74].

Paper VI was carried out with the aim to find a novel titanium phosphate based (Ti-P) heterogeneous catalyst for epoxidation of methyl esters from waste cooking oils, which would achieve high conversion of esters and low selectivity to oxirane cleavage products. The catalysts were synthesized from various sources of titanium and structure directing agents based on paper [75]. Furthermore, other conventionally used catalysts for epoxidation were synthesized for comparison: (i) Ti-MCM-41 based on paper [76], (ii) Ti-SBA-15 according to [77], and (iii) Ti-AlP based on [78]. Moreover, TS-1 as a standard industrial catalyst was purchased for comparison.

The composition of catalysts was determined by XRF. The Ti content in TS-1, Ti-MCM-41 and Ti-SBA-15 was 1.75, 1.47, and 2.13 wt.%, respectively, whereas the content of Si was the same in all catalysts (45.0-45.2 wt.%). The catalyst Ti-AlP contained 5.25 wt.% of Ti, 21.4 wt.% of Al, 18.4 wt.% of P, and approximately 8.2 wt.% of chloride (residues from its synthesis). The Ti content in Ti-P catalysts varied from 29.2 wt.% to 31.3 wt.%, and P content varied from 18.4 wt.% to 22.2 wt.%.

Catalyst synthesis was confirmed by XRD. TS-1 showed the SiO_2 signal, while Ti-AlP contained boehmite and NH_4Cl impurities (Fig. 11A). Ti-MCM-41 and Ti-SBA-15 displayed typical low-angle peaks (Figs. 11B, 11C); Ti-SBA-15 also showed ZrO_2 and anatase TiO_2, which is undesirable due to H_2O_2 decomposition [79]. In Ti-P (Fig. 11D), peaks indicated $H_2Ti_3O_7$ and $Ti(HPO_4)_2$.

A UV-VIS method was employed to monitor the oxidative state of titanium species in catalysts (Fig. 12). Literature research revealed that only Ti in an oxidative state IV^+ is active in epoxidation [80, 81]. The method allows to quantify the amount of Ti(IV) species through an absorption band at 205-220 nm. Other absorption bands, such as 250-290 nm belong to Ti(V) and Ti(VI) [82], whereas band at 310-330 nm belongs to anatase phase of TiO_2 [83]. The presence of both these absorption bands is undesirable, as these Ti forms are inactive in epoxidation, or promote H_2O_2 decomposition, respectively. The analysis revealed that TS-1 catalyst had only Ti(IV) species, however, its intensity was the lowest among all the catalysts. Catalyst Ti-MCM-41 active sites were predominantly composed of Ti(V) and Ti(VI) species, which is undesirable for epoxidation. Catalysts Ti-SBA-15 and Ti-AlP had similar profiles with Ti(IV) and Ti(V) + Ti(VI) active sites being of similar intensities. All Ti-P catalysts had a very similar UV-VIS spectra, where all Ti species (IV, V, VI and the anatase phase) were observed.

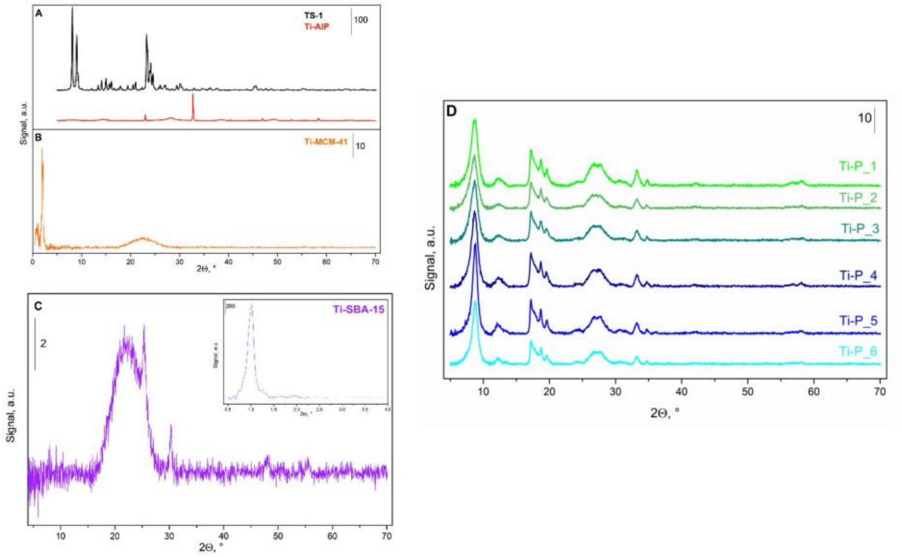

Fig. 11: *Diffractograms of synthesized titanium catalysts*

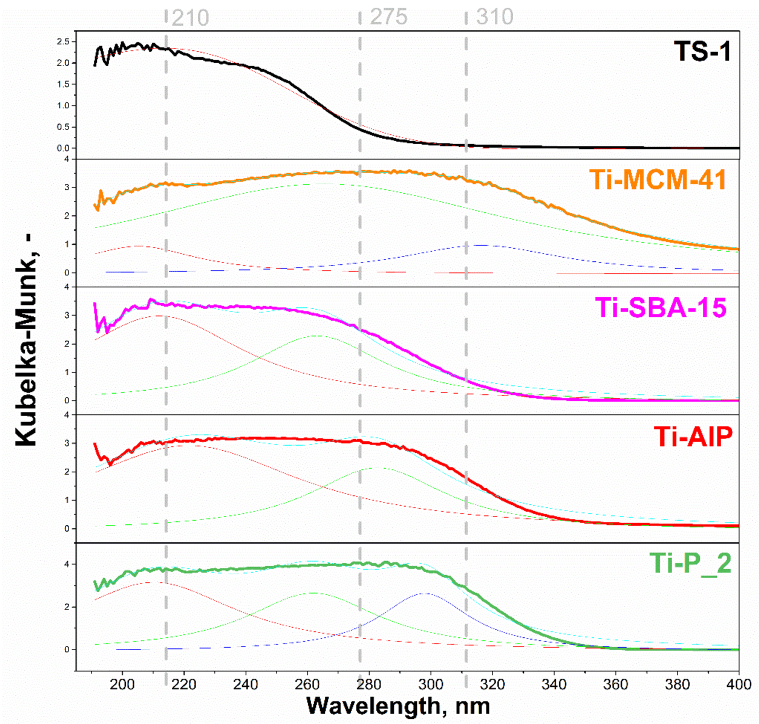

Fig. 12: *Results of UV-VIS measurements*

Next, mercury porosimetry was applied to study the morphology of catalysts (pore size distribution, area of pores, and porosity). This method is suitable for description of meso- and macro-pores, which is favourable, as large methyl ester molecules are epoxidized. The measurements revealed that Ti-SBA-15 and Ti-MCM-41 (Fig. 13A) are mesoporous materials with an average pore diameter of 4-5 and 10-15 nm, respectively. The pore diameters of TS-1 and Ti-AlP catalysts were determined at around 50 nm. All Ti-P catalysts had a similar desorption curves with an increasing pore diameter up to around 500 nm (Fig. 13B). This indicates that the material is macroporous, and therefore should be suitable for epoxidation of large methyl ester molecules.

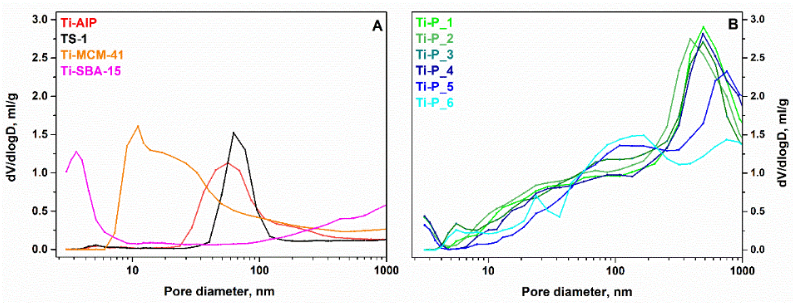

Fig. 13: *Results of Hg-porosimetry measurements*

At last, the catalysts were tested in an epoxidation of methyl esters from waste cooking oils. The reaction was carried out at 50 °C for 24 h. Approximately 1.5 g of ME was used with 1.5 g of H_2O_2, 30 wt.% catalyst, and acetonitrile as a solvent. Conversion of methyl esters and selectivity to nonanal (as the main product of oxirane bond cleavage [84]) were monitored.

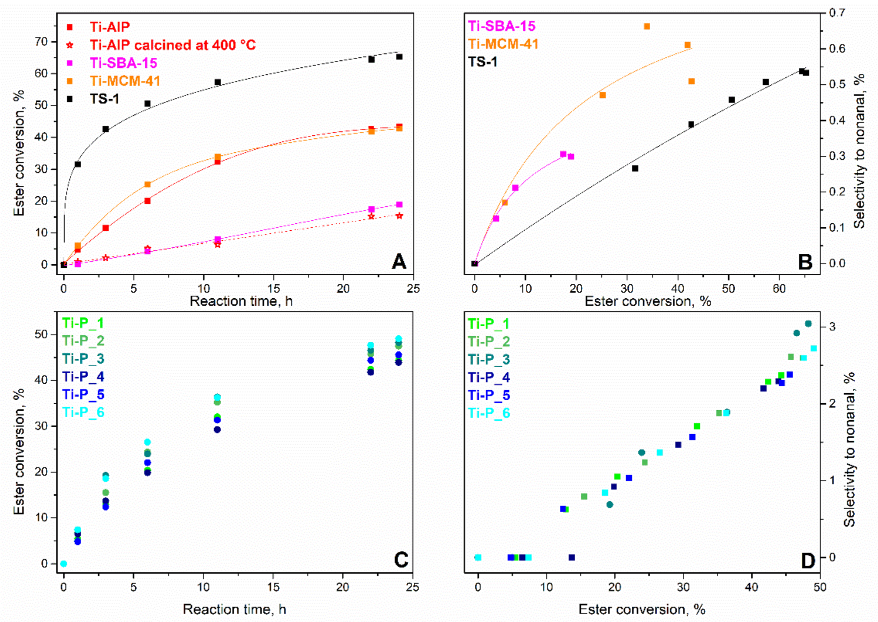

Fig. 14: *Results of catalytic testing for various catalysts*

The lowest ester conversion (approximately 19% after 24 h) was observed for Ti-SBA-15 catalyst (Fig. 14A). The reason for that is probably small pore diameter (Fig. 13A). The pores were probably difficult to access by large methyl ester molecules (their size is approximately 3-4 nm) [85]. Furthermore, ME molecules are usually in a cis- conformation (they are curved), pores are probably not straight (but of an irregular shape), and the double bond in the middle of the carbon chain of methyl esters has to be correctly oriented with an active site and H_2O_2 molecule. Therefore, the reaction probably proceeded on the surface of the catalyst, where small amounts of Ti(IV) are located, rather than in its pores. The conversion of methyl esters for Ti-MCM-41 and Ti-AlP was the same (approximately 43% after 24 h, Fig. 14A). This relatively low conversion was probably caused by the presence of Ti(V) and Ti(VI), which are inactive in epoxidation. However, selectivity to nonanal was increasing with an increasing ME conversion up to 0.7% for Ti-MCM-41, whereas nonanal was not detected in case of Ti-AlP (Fig. 14B). Furthermore, Ti-AlP catalyst had been also calcined at 400 °C and used in epoxidation, because this procedure is usually applied by other authors. However, in paper VI the achieved ME conversion was only 15% after 24 h, which was different compared to other papers [86, 87]. The Ti-P catalysts had not been calcined before epoxidation (because of their similar properties to Ti-AlP materials) to avoid low conversions of methyl esters.

Afterwards, commercial TS-1 catalyst was employed for comparison. The highest conversion (approximately 65% after 24h) was achieved with a relatively small selectivity to nonanal (0.5%), Fig. 14A and 14B, respectively. High activity can be explained by the high amount of Ti(IV) species, which promote epoxidation. On the contrary, profiles of conversion of ME on reaction time were very similar for all Ti-P materials, regardless of the chemicals they had been synthesized from. The maximum methyl esters conversion of 49 % (Fig. 14C) was observed after 24 h with Ti-P_6. Furthermore, the selectivity to nonanal increased with an increasing methyl esters conversion and reached a maximum of approximately 2.7 % (Fig. 14D).

The most active Ti-P_6 catalyst was employed for a scale-up epoxidation in a 6 l reactor. This is a novelty, as authors in other papers usually carry out the epoxidation in small amounts. The amount of catalyst was increased to 180 g, whereas all other molar ratios were kept the same as in the reaction in smaller reactor. The conversion of ME reached 71 % after 48 h of reaction time with the selectivity to nonanal reaching 2.0 %, which was slightly lower than in a small-scale epoxidation, and was probably influenced by chemical engineering parameters (such as stirring, diffusion, etc.). Moreover, the leaching of Ti to the reaction mixture was measured after 48 h of reaction time, and only 0.025 wt.% of Ti was determined by ICP. Furthermore, epoxy index of 2.55 mol/kg was determined in the reaction mixture, which confirmed successful formation of epoxides from WCO methyl esters. Moreover, the formation of epoxide products was confirmed by simulated distillation.

In conclusion, the new titanium-phosphate materials were successfully employed in an epoxidation of ME from waste cooking oils (49 % ME conversion) compared to commercially used TS-1 material (65% ME conversion). Furthermore, the scale-up was successful, and 70 % ME conversion was achieved after 48 h of reaction time. However, vast amouns of acetonitrile solvent are required for the reaction to proceed. Further research is recommended to minimize the amount of solvent consumption and to tune the properties of Ti-P materials to obtain higher yields of products.

4 Conclusion

The disertation thesis was focused on preparation of methyl esters from various vegetable and their application in epoxidation. In the first part, homogeneous (KOH) and heterogeneous (MgAl mixed oxides) catalysts were employed in transesterification. In the second part, the epoxidation process of methyl esters from various vegetable oils was studied.

First, methyl and butyl esters from various vegetable oils were prepared by homogeneous transesterification (KOH). The influence of three methods of reaction quenching on ester losses (leaching into glycerol phase) were studied. The losses of butyl esters were higher than losses of methyl esters independent on the way of reaction quenching. Fatty acid profiles of butyl esters were consistent, while methyl esters of linolenic acid favored the glycerol phase. The losses of methyl esters varied for CO_2 stopping and phosphoric acid stopping from oil to oil. Moreover, high pH (>10) and higher ionic strength increased content of linolenic acid esters in glycerol phase.

The second study examined how sodium residues in Mg-Al mixed oxides affect their properties and methyl ester yield. More residue sodium decreased overall basicity and decreased the amount of medium strong basic centres at the expense of an increase in the amount of weak basic sites. The highest yield of methyl esters was achieved with the least washed materials because Na_2O (from $NaNO_3$ decomposition) formed NaOH with water in methanol, promoting homogeneous catalysis and increased yield. This was proved by addition of $NaNO_3$ to mixed oxides before their synthesis.

Homogeneous epoxidations of methyl esters from various oils were carried out and suitable analytical methods for identification of individual reaction products were found. IR-ATR was used to monitor: (i) degree of oxirane bond cleavage, (ii) conversion of double bonds, and (iii) formation of epoxides. The HPLC-RI separated products of epoxidation according to the length of their carbon chain and presence/absence of an epoxide bond. The GC-MS method was used to identify epoxides of methyl esters with different fatty acid profiles and various degrees of epoxidation. Furthermore, this method was used for quantification of individual reaction products.

In next two papers, the homogeneous epoxidation of methyl esters of *Camelina sativa,* rapeseed and linseed oil was thoroughly described. The relationships between reaction conditions and properties of products were explained using principal component analysis. Higher reaction time and temperature were favourable for the epoxidation, whereas the presence of H_2SO_4 was undesirable (oxirane bond cleavage took place). The homogeneous epoxidation process of methyl esters of linseed and rapeseed oil was optimized in terms of reaction conditions and a series of mathematical equations that allow to tune the properties of products before their synthesis was obtained. Furthermore, thermodynamic parameters (ΔG, ΔH) were calculated using quantum chemistry calculations. The most favourable order of epoxidation of double bonds for individual molecules was described.

Novel catalysts based on Ti-P materials were synthesized, characterized, and used in a heterogeneous epoxidation of methyl esters of waste cooking oils. The oxidative state of Ti species was studied by UV-VIS. The porosity and distribution of pores was studied by mercury porosimetry. The materials were compared with conventionally used catalysts for epoxidation. A 50% conversion of methyl esters was achieved with novel Ti-P catalysts, whereas the best performing commercial catalyst achieved 65% conversion. Furthermore, Ti-P catalysts were successfully employed in a scale-up epoxidation with 70% conversion of methyl esters.

List of Published Works:

Paper I: Aleš Vávra, Martin Hájek, **David Kocián**, *The influence of vegetable oils composition on separation of transesterification products, especially quality of glycerol*, Renewable Energy, Volume 176, 2021, https://doi.org/10.1016/j.renene.2021.05.050, (IF = 8.6; Q1)

Paper II: David Kocián, Martin Hájek, Karel Frolich, Jaroslav Kocík, *The influence of residue sodium ions in mixed oxide on catalytic activity in transesterification of vegetable oil*, Molecular catalysis, Vol. 517, 2022, https://doi.org/10.1016/j.mcat.2021.112017, (IF = 4.6; Q2)

Paper III: Martin Hájek, Tomáš Hájek, **David Kocián**, Karel Frolich, András Peller, *Epoxidation of Methyl Esters as Valuable Biomolecules: Monitoring of Reaction*, Molecules, Vol. 28, 2023, https://doi.org/10.3390/molecules28062819, (IF = 4.2; Q2)

Paper IV: Martin Hájek, **David Kocián**, Tomáš Hájek, Vladimír Lukeš, Erik Klein, *Epoxidation of Camelina sativa oil methyl esters as a second-generation biofuel with thermodynamic calculations*, Renewable Energy, Vol. 228, 2024, https://doi.org/10.1016/j.renene.2024.120670, (IF = 9.0, Q1)

Paper V: Martin Hájek, **David Kocián**, Miroslav Douda, *Statistical evaluation of the epoxidation of esters from vegetable oils and optimization of reaction conditions*, Renewable energy, Vol. 213, 2023, https://doi.org/10.1016/j.renene.2023.05.061, (IF = 8.7; Q1)

Paper VI: Jaroslav Kocík, Zdeněk Tišler, Martin Hájek, **David Kocián**, *The influence of titanium on formation of bio-epoxides from esters synthesis from waste vegetable oil,* Clean Technologies and Environmental Policy, 2025 (IF = 3.9; Q2) - accepted manuscript (22.7.2025)

5 References

[1] H. Ritchie, P. Rosado, M. Roser, Energy production and consumption, 2020. 'https://ourworldindata.org/energy-production-consumption' (Accessed 7.7. 2025).
[2] REN21, GSR 2024 Global Overview, 2024. https://www.ren21.net/wp-content/uploads/2019/05/GSR2024_GlobalOverview_Full_Report_with_endnotes_web.pdf. (Accessed 7.7. 2025).

[3] A.K. Chandel, V.K. Garlapati, A.K. Singh, F.A.F. Antunes, S.S. da Silva, The path forward for lignocellulose biorefineries: Bottlenecks, solutions, and perspective on commercialization, Bioresource Technol 264 (2018) 370-381.
[4] O.H.K. Adhari, M. Mahmoud, M.A. Abdelkareem, A.G. Olabi, Comprehensive Green Materials, 1.23 - Green Hydrogen Production: Energy and Exergy Analysis, First Edition ed.2025.
[5] M.M. Kucuk, A. Demirbas, Biomass conversion processes, Energ Convers Manage 38(2) (1997) 151-165.
[6] C.R.V. Matheus, L.H. Chagas, G.G. Gonzalez, E.F.S. Aguiar, L.G. Appel, Synthesis of Propene from Ethanol: A Mechanistic Study, Acs Catal 8(8) (2018) 7667-7678.
[7] M.D. Bruyn, Z. Sun, K. Barta, Advances in Inorganic Chemistry, Chapter Three - The thousand faces of Cu-doped porous mixed oxides (Cu-PMO) in the conversion of renewable resources and beyond, 2021.
[8] T. Bhaskar, A. Pandey, Recent Advances in Thermo-Chemical Conversion of Biomass, Chapter 1 - Advances in Thermochemical Conversion of Biomass—Introduction, 2015.
[9] B. Volynets, F. Ein-Mozaffari, Y. Dahman, Biomass processing into ethanol: pretreatment, enzymatic hydrolysis, fermentation, rheology, and mixing, Green Process Synth 6(1) (2017) 1-22.
[10] H.J. Kurji, M.S. Imran, A.S. Bded, The impact of using pure ethanol additives on gasoline fuel with respect to SI engine emissions, IOP Conference Series: Materials Science and Engineering 1067(1) (2021) 012090.
[11] N.E. Selin, C. Lehman, Biofuel, 2025. https://www.britannica.com/technology/biofuel. (Accessed 7.7. 2025).
[12] H. Naveed, A. H. Al-Muhtaseb, F. Jamil, S. Al-Maawali, R. Al-Hajri, Environmental Sustainability of Biofuels, Chapter 9 - Prospects of R&D in the biofuel sector/industry, 2023.
[13] E.C. Bensah, M. Mensah, Chemical Pretreatment Methods for the Production of Cellulosic Ethanol: Technologies and Innovations, Int J Chem Eng 2013 (2013).
[14] D.F. Correa, H.L. Beyer, H.P. Possingham, S.R. Thomas-Hall, P.M. Schenk, Biodiversity impacts of bioenergy production: Microalgae vs. first generation biofuels, Renew Sust Energ Rev 74 (2017) 1131-1146.
[15] T.G. Tornabene, G. Holzer, S. Lien, N. Burris, Lipid-Composition of the Nitrogen Starved Green-Alga Neochloris-Oleoabundans, Enzyme Microb Tech 5(6) (1983) 435-440.
[16] P.T. Vasudevan, M. Briggs, Biodiesel production-current state of the art and challenges, J Ind Microbiol Biot 35(5) (2008) 421-430.
[17] C. Lehman, Biodiesel, 2025. https://www.britannica.com/technology/biodiesel. (Accessed 7.7. 2025).
[18] K. Patel, S.K. Singh, Environmental sustainability analysis of biofuels: a critical review of LCA studies, Clean Technol Envir (2023).
[19] O.M. Ali, R. Mamat, M.G. Rasul, G. Najafi, Chapter Eighteen - Potential of Biodiesel as Fuel for Diesel Engine, (2017) 557-590.
[20] F.S. Li, Z.W. Liu, Z.H. Ni, H. Wang, Effect of biodiesel components on its lubrication performance, J Mater Res Technol 8(5) (2019) 3681-3687.
[21] Alternative fuels data center, Biodiesel Benefits and Considerations. https://afdc.energy.gov/fuels/biodiesel-benefits. (Accessed 7.7. 2025).
[22] W.N.M.W. Ghazali, R. Mamat, H.H. Masjuki, G. Najafi, Effects of biodiesel from different feedstocks on engine performance and emissions: A review, Renew Sust Energ Rev 51 (2015) 585-602.
[23] J.A. Kinast, Production of Biodiesels from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/Diesel Blends: Final Report; Report 1 in a Series of 6, (2003).
[24] J.F. Sun, J.A. Caton, T.J. Jacobs, Oxides of nitrogen emissions from biodiesel-fuelled diesel engines, Prog Energ Combust 36(6) (2010) 677-695.
[25] W. Wilms, J. Homa, M. Wozniak-Karczewska, M. Owsianiak, L. Chrzanowski, Biodegradation half-lives of biodiesel fuels in aquatic and terrestrial systems: A review, Chemosphere 313 (2023).
[26] M. Mahdavi, E. Abedini, A. Darabi, Biodiesel synthesis from oleic acid by nano-catalyst (ZrO2/Al2O3) under high voltage conditions, RSC Advances 5(68) (2015) 55027-55032.

[27] D. Singh, D. Sharma, S.L. Soni, S. Sharma, K.S. Pushpendra, A. Jhalani, A review on feedstocks, production processes, and yield for different generations of biodiesel, Fuel 262 (2020) 116553.
[28] S. Park, T.H.T. Nguyen, E. Jin, Improving lipid production by strain development in microalgae: Strategies, challenges and perspectives, Bioresource Technol 292 (2019).
[29] N.K. Patel, S.N. Shah, Food, Energy, and Water, 11 - Biodiesel from Plant Oils, 2015.
[30] Y.L. Gu, F. Jérôme, Glycerol as a sustainable solvent for green chemistry, Green Chem 12(7) (2010) 1127-1138.
[31] H.W. Tan, A.R.A. Aziz, M.K. Aroua, Glycerol production and its applications as a raw material: A review, Renew Sust Energ Rev 27 (2013) 118-127.
[32] X.S. Zhang, G.X. Yang, H. Jiang, W.J. Liu, H.S. Ding, Mass production of chemicals from biomass-derived oil by directly atmospheric distillation coupled with co-pyrolysis, Sci Rep-Uk 3 (2013).
[33] W.N.A.W. Osman, M.H. Rosli, W.N.A. Mazli, S. Samsuri, Comparative review of biodiesel production and purification, Carbon Capture Sci T 13 (2024).
[34] M. Ostojcic, S. Brkic, M. Tisma, B. Zelic, S. Budzaki, Membrane Filtration as an Environmentally Friendly Method for Crude Biodiesel Purification, Kem Ind 69(3-4) (2020) 175-181.
[35] R. Nayab, M. Imran, M. Ramzan, M. Tariq, M.B. Taj, M.N. Akhtar, H.M.N. Iqbal, Sustainable biodiesel production via catalytic and non-catalytic transesterification of feedstock materials-A review br, Fuel 328 (2022).
[36] X.L. Miao, R.X. Li, H.Y. Yao, Effective acid-catalyzed transesterification for biodiesel production, Energ Convers Manage 50(10) (2009) 2680-2684.
[37] M. Melchiorre, R. Amendola, V. Benessere, M.E. Cucciolito, F. Ruffo, R. Esposito, Solvent-free transesterification of methyl levulinate and esterification of levulinic acid catalyzed by a homogeneous iron(III) dimer complex, Mol Catal 483 (2020).
[38] R.Y. Rao, P.K. Zubaidha, D.D. Kondhare, N.J. Reddy, S.S. Deshmukh, Biodiesel production from seed oil using crystalline manganese carbonate, Pol J Chem Technol 14(1) (2012) 65-70.
[39] P. Felizardo, M.J.N. Correia, I. Raposo, J.F. Mendes, R. Berkemeier, J.M. Bordado, Production of biodiesel from waste frying oil, Waste Manage 26(5) (2006) 487-494.
[40] G. Vignesh, D. Barik, Energy from Toxic Organic Waste for Heat and Power Generation, Chapter 6 - Toxic Waste From Biodiesel Production Industries and Its Utilization, 2019.
[41] N. Gutiérrez-Ortega, E. Ramos-Ramírez, A. Serafín-Muñoz, A. Zamorategui-Molina, J. Monjaraz-Vallejo, Use of Co/Fe-Mixed Oxides as Heterogeneous Catalysts in Obtaining Biodiesel, Catalysts 9(5) (2019).
[42] Y.S. Lu, Z.W. Zhang, Y.F. Xu, Q. Liu, G.R. Qian, CaFeAl mixed oxide derived heterogeneous catalysts for transesterification of soybean oil to biodiesel, Bioresource Technol 190 (2015) 438-441.
[43] C.F. Hansen, A. Hernandez, B.P. Mullan, K. Moore, M. Trezona-Murray, R.H. King, J.R. Pluske, A chemical analysis of samples of crude glycerol from the production of biodiesel in Australia, and the effects of feeding crude glycerol to growing-finishing pigs on performance, plasma metabolites and meat quality at slaughter, Anim Prod Sci 49(2) (2009) 154-161.
[44] H. Pang, G.J. Yang, L. Li, J.H. Yu, Efficient transesterification over two-dimensional zeolites for sustainable biodiesel production, Green Energy Environ 5(4) (2020) 405-413.
[45] A.M. Lauermannová, I. Paterová, J. Patera, K. Skrbek, O. Jankovsky, V. Bartunek, Hydrotalcites in Construction Materials, Appl Sci-Basel 10(22) (2020).
[46] A. Ruz-Luna, M. Cruz-Yusta, M. Sánchez, L. Sánchez, B. Gámiz, I. Pavlovic, Dual function of ultra-laminated hydrotalcite in environmental remediation: Adsorption of water contaminant BP-4 and reutilization of the adsorption product for photocatalytic NOx air decontamination, J Environ Chem Eng 12(1) (2024).
[47] D. Suescum-Morales, J.R. Jiménez, J.M. Fernández-Rodríguez, Review of the Application of Hydrotalcite as CO2 Sinks for Climate Change Mitigation, Chemengineering 6(4) (2022).
[48] S. Rackley, Negative Emissions Technologies for Climate Change Mitigation, Chapter 8 - CO2 adsorption, 2023.
[49] A.I.M. Rabee, J.C. Manayil, M.A. Isaacs, C.M.A. Parlett, L.J. Durndell, M.I. Zaki, A.F. Lee, K. Wilson, On the Impact of the Preparation Method on the Surface Basicity of Mg-Zr Mixed Oxide Catalysts for Tributyrin Transesterification, Catalysts 8(6) (2018).

[50] L. Dubnová, L. Smoláková, O. Kikhtyanin, J. Kocík, D. Kubicka, M. Zvolská, M. Pouzar, L. Capek, The role of ZnO in the catalytic behaviour of Zn-Al mixed oxides in aldol condensation of furfural with acetone, Catal Today 379 (2021) 181-191.
[51] L. Obalová, Materiály na bázi hydrotalcitu pro katalytický rozklad N2O, Ostrava : Vysoká škola báňská - Technická univerzita, Fakulta metalurgie a materiálového inženýrství (2008).
[52] T. Eryilmaz, M.K. Yesilyurt, C. Cesur, O. Gokdogan, Biodiesel production potential from oil seeds in Turkey, Renew Sust Energ Rev 58 (2016) 842-851.
[53] M. Malisova, M. Hajek, D. Kocian, J. Malina, A. Peller, M. Hornacek, The influence of various anions in Mg-Al mixed oxides on presence of sodium ions in transesterification of oil, Fuel 319 (2022).
[54] V.M. Abbasov, F.A. Nasirov, N.S. Rzayeva, L.I. Nasirova, K.Z. Musayeva, Epoxidated Vegetable Oils: Preparation, Properties and Application, Process Petrochem Oi 19(4) (2018) 427-449.
[55] Z.S. Lin, Y.R. Zhang, C.K. Ober, J.M. Goddard, Facile Preparation of Epoxide-Functionalized Surfaces via Photocurable Copolymer Coatings and Subsequent Immobilization of Iminodiacetic Acids, Acs Appl Mater Inter 10(47) (2018) 40871-40879.
[56] V.C. Malshe, G. Waghoo, Weathering study of epoxy paints, Prog Org Coat 51(4) (2004) 267-272.
[57] L.H. Hu, W. Xu, Q. Jiang, R.Y. Ji, Z.C. Yan, G.D. Wu, Recent progress on CO2 cycloaddition with epoxide catalyzed by ZIFs and ZIFs-based materials, J Co2 Util 81 (2024).
[58] W.P. Liu, T. Leischner, W. Li, K. Junge, M. Beller, A General Regioselective Synthesis of Alcohols by Cobalt-Catalyzed Hydrogenation of Epoxides, Angew Chem Int Edit 59(28) (2020) 11321-11324.
[59] F.L. Jin, X. Li, S.J. Park, Synthesis and application of epoxy resins: A review, J Ind Eng Chem 29 (2015) 1-11.
[60] J.J. Cai, Z.Y. Wu, N.F. Gao, H.S. Xu, D.M. Wang, F. Zhou, Y. Nie, Novel packed bed reactor designed for Prileschajew epoxidation of fatty acid methyl ester: Intensification of mass/heat transfer, Chem Eng Process 176 (2022).
[61] B.R. Moser, S.C. Cermak, K.M. Doll, J.A. Kenar, B.K. Sharma, A review of fatty epoxide ring opening reactions: Chemistry, recent advances, and applications, J Am Oil Chem Soc 99(10) (2022) 801-842.
[62] E. Nadim, P. Paraskar, H. Moradi, M. Hesabi, Y.S. Qiao, E.J. Murphy, I. Major, Kinetic and thermodynamic analysis of hemp oil epoxidation with density functional theory insights into unsaturated fatty acid epoxidation and ring-opening reactions, Chem Eng J Adv 22 (2025).
[63] J. La Scala, R.P. Wool, Effect of FA composition on epoxidation kinetics of TAG, J Am Oil Chem Soc 79(4) (2002) 373-378.
[64] L.M. Ramirez, J.G. Cadavid, A. Orjuela, M.F. Gutierrez, W.F. Bohorquez, Epoxidation of used cooking oils: Kinetic modeling and reaction optimization, Chem Eng Process 176 (2022).
[65] A.H. Suzuki, B.G. Botelho, L.S. Oliveira, A.S. Franca, Sustainable synthesis of epoxidized waste cooking oil and its application as a plasticizer for polyvinyl chloride films, Eur Polym J 99 (2018) 142-149.
[66] A. Obour, H. Sintim, E. Obeng, V. Jeliazkov, Oilseed Camelina (Camelina sativa L Crantz): Production Systems, Prospects and Challenges in the USA Great Plains, Advances in Plants & Agriculture Research 2 (2015).
[67] C. Orellana-Coca, D. Adlercreutz, M.M. Andersson, B. Mattiasson, R. Hatti-Kaul, Analysis of fatty acid epoxidation by high performance liquid chromatography coupled with evaporative light scattering detection and mass spectrometry, Chem Phys Lipids 135(2) (2005) 189-199.
[68] B. Rangarajan, A. Havey, E.A. Grulke, P.D. Culnan, Kinetic parameters of a two-phase model forin situ epoxidation of soybean oil, Journal of the American Oil Chemists' Society 72(10) (1995) 1161-1169.
[69] A. Campanella, M.A. Baltanás, Degradation of the oxirane ring of epoxidized vegetable oils with solvated acetic acid using cation-exchange resins, Eur J Lipid Sci Tech 106(8) (2004) 524-530.
[70] P. Dong, T.N. Shao, J.L. Li, X.H. Zhang, Y. Zhao, X.H. Zhao, G.X. Li, An Overview of Heterogeneous Transition Metal-Based Catalysts for Cyclohexene Epoxidation Reaction, Eur J Inorg Chem (2023).
[71] Y.R. Shen, P.P. Jiang, P.T. Wai, Q. Gu, W.J. Zhang, Recent Progress in Application of Molybdenum-Based Catalysts for Epoxidation of Alkenes, Catalysts 9(1) (2019).

[72] T. Zhang, L. Mazaud, L.M. Chamoreau, C. Paris, A. Proust, G. Guillemot, Unveiling the Active Surface Sites in Heterogeneous Titanium-Based Silicalite Epoxidation Catalysts: Input of Silanol-Functionalized Polyoxotungstates as Soluble Analogues, Acs Catal 8(3) (2018) 2330-2342.
[73] J. Kocík, Z. Tisler, M. Hájek, K. Peroutková, J. Simek, K. Strejcová, J. Malina, Epoxidation of methyl esters from waste vegetable oil by heterogeneous catalysts WO3/Al2O3, Mol Catal 569 (2024).
[74] J.M. Yang, S.L. Liu, Y.Y. Liu, L.M. Zhou, H. Wen, H.J. Wei, R.F. Shen, X.L. Wu, J.C. Jiang, B.J. Li, Review and perspectives on TS-1 catalyzed propylene epoxidation, Iscience 27(3) (2024).
[75] A. Bhaumik, Mesoporous titanium phosphates and related molecular sieves: Synthesis, characterization and applications, P Indian as-Chem Sci 114(4) (2002) 451-460.
[76] S. Ghodke, R. Patel, U. Chudasama, Mesoporous Zr-MCM-41 and Ti-MCM-41 as Solid Oxidation Catalysts in the synthesis of Epichlorohydrin, 3297 (2007).
[77] A. Wróblewska, P. Miadlicki, J. Srenscek-Nazzal, M. Sadlowski, Z.C. Koren, B. Michalkiewicz, Alpha-pinene isomerization over Ti-SBA-15 catalysts obtained by the direct method: The influence of titanium content, temperature, catalyst amount and reaction time, Micropor Mesopor Mat 258 (2018) 72-82.
[78] H.-X. Li, M.E. Davis, Chapter 4 Phosphate-based molecular sieves with pores comprised of greater than 12-rings, Catal Today 19(1) (1994) 61-106.
[79] C.W. Yoon, K.F. Hirsekorn, M.L. Neidig, X.Z. Yang, T.D. Tilley, Mechanism of the Decomposition of Aqueous Hydrogen Peroxide over Heterogeneous TiSBA15 and TS-1 Selective Oxidation Catalysts: Insights from Spectroscopic and Density Functional Theory Studies, Acs Catal 1(12) (2011) 1665-1678.
[80] F. Bonino, A. Damin, G. Ricchiardi, M. Ricci, G. Spanò, R. D'Aloisio, A. Zecchina, C. Lamberti, C. Prestipino, S. Bordiga, Ti-peroxo species in the TS-1/H2O2/H2O system, J Phys Chem B 108(11) (2004) 3573-3583.
[81] M. Guidotti, N. Ravasio, R. Psaro, E. Gianotti, L. Marchese, S. Coluccia, Heterogeneous catalytic epoxidation of fatty acid methyl esters on titanium-grafted silicas, Green Chem 5(4) (2003) 421-424.
[82] N. Mizuno, Modern Heterogeneous Oxidation Catalysis: Design, Reactions and Characterization, Wiley (2009).
[83] Y. Zuo, M. Liu, X. Guo, Stability and Applications of Coordination Compounds - Chapter 9 - Coordination States and Catalytic Performance of Ti in Titanium Silicalite-1, London, 2020.
[84] M.Z. Lu, L.B. Peng, Q.L. Xie, Y. Nie, X.J. Liu, X.H. Lu, J.B. Ji, Oxidative Cleavage of Methyl 9,10-Epoxystearate over WO3/MCM-41 for Methyl 9-Oxononanoate Production, Eur J Lipid Sci Tech 120(7) (2018).
[85] W.F. Hölderich, L.A. Rios, P.P. Weckes, H. Schuster, Process for the production of epoxidized oleochemicals. , Germany, 2004.
[86] J. Prech, J. Cejka, UTL titanosilicate: An extra-large pore epoxidation catalyst with tunable textural properties, Catal Today 277 (2016) 2-8.
[87] J. Prech, M. Kubu, J. Cejka, Synthesis and catalytic properties of titanium containing extra-large pore zeolite CIT-5, Catal Today 227 (2014) 80-86.