

Selective Oxidative Cleavage of Oleic Acid on Alumina Supported Metal Catalyst

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Abstract Short-chain fatty acids (SCFAs) and medium-chain fatty acid (MCFAs) are valuable raw materials in wide range of chemical and medical applications. They can be converted to other derivatives by known chemical reactions. Unfortunately, both SCFAs MCFAs are not as abundant in nature as long-chain fatty acid (LCFAs). In this work, the oxidative cleavage of oleic acid, which is one of the most abundant unsaturated LCFAs in nature, was studied. The oxidation was induced by hydrogen peroxide catalyzed by a commercial alumina-supported metal catalyst. The products were analyzed by gas chromatography equipped with mass spectroscopy (GC/MS). The results revealed that MCFAs and SCFAs were detected in a product. In addition, aldehydes were also found. In this work, effects of catalyst loading, oleic acid-to-hydrogen peroxide ratio, reaction time were investigated and reported.

1 Introduction

Nowadays, fats and oil have become more attractive resource as renewable raw materials in oleochemical industries. Unsaturated fatty acids (UFAs), which are abundantly available in nature as the complement of lipids, can be used as a substrate to produce medium-chain fatty acids (MCFAs) and short-chain fatty acids (SCFAs). Generally, these fatty acids are valuable materials and widely used for different industrial applications, such as being used as an intermediates in the production of food preservatives (Gopinger *et al.*, 2015), herbicides, medicines (Ihre *et al.*, 1996), food production, fragrant (Armstrong and Yamazaki, 1986), antibiotic compounds (Huang *et al.*, 2011), biofuels (Yanowitz *et al.*, 2011), lubricants, and plasticizers (Noureddini and Rempe, 1996) (Turnwald *et al.*, 1998). Moreover, short-chain fatty acids can also be converted to other derivatives by chemical reaction to produce biofuels that are environmentally friendly. It is considered that short-chain fatty acids are one of the important building blocks in oleochemical industry.

Generally, SCFAs and MCFAs are obtained from separation of vegetable oils or animal fats. Unfortunately, both SCFAs MCFAs are not as abundant in nature as LCFAs, hence, they are difficult to be separated from the oil. Although SCFAs and MCFAs could be synthesized from petroleum products and natural gas (Spargo, 2003), the process is not only complex and costly, but also contains contaminated residue that makes it unsuitable for consumption.

This research proposes a method to produce SCFAs and MCFAs from LCFAs by oxidation cleavage reaction. In general, the cleavage of carbon-carbon double bond in UFAs following by the oxidation of the cleaved products results in mono- and di- carboxylic acids as shown in Figure 1 (Godard *et al.*, 2016). In industrial scale, oxidative cleavage of UFAs has been developed using ozone as oxidizing agent. Due to hazardous issue, using ozone is not sustainable. Alternative oxidizing agent such as hydrogen peroxide (H₂O₂) has been studied instead of ozone since it has advantage in not only environmental reasons, but also in economic reasons.

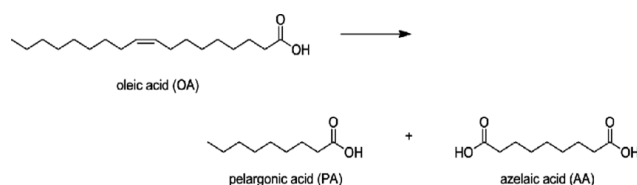


Figure 1. Oxidative cleavage of oleic acid

Transition metals have been used as catalyst for oxidation at mild condition. Several transition metals such as Os, Co, Mo, Mn, Fe, Ru, and W have been investigated for this purpose and have been reported in review paper (Enferadi Kerenkan *et al.*, 2016a). Although homogeneous catalysts have shown excellent

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performance in oxidation of UFAs (Khlebnikova *et al.*, 2009), they are associated with lack of catalyst recovery. For heterogeneous catalysts, high surface area is needed to enhance contact between the liquid substrate and the solid catalyst (Enferadi Kerenkan *et al.*, 2016a). To achieve such high surface area, mesoporous structure have been employed (Enferadi Kerenkan *et al.*, 2016b). In this work, effects of catalyst loading, oleic acid-to-hydrogen peroxide ratio, and reaction time were investigated and reported.

2. Experimental

2.1 Materials

Oleic acid (C₁₈H₃₄O₂, 98% purity, extrapure grade), hydrogen peroxide (H₂O₂, 30% v/w, AR grade), methyl alcohol (CH₃OH, AR grade), hexane (C₆H₁₄, AR grade), and hydrochloric acid (HCl, 37% v/w, AR grade) were provided from QReC. Tert-butyl alcohol ((CH₃)₃COH, AR grade) was provided from LobaChemie. Sodium sulfate (Na₂SO₄, AR grade) was provided from Fisherchemical. The commercial catalysts supported on alumina (1%, 10% Loading) were supplied from Liaoning Haitai Sci-Tech Development Co., Ltd. Standard of methyl oleate (C₁₉H₃₆O₂, 1000 µg/ml in hexane), methyl nanoate (C₁₀H₁₈O₂, 1000 µg/ml in hexane), dimethyl azelate (C₁₁H₂₀O₄, 1000 µg/ml in hexane) were provided from AccuStandard. All chemical reagents were used without further purification.

2.2 Characterization

The specific surface area (BET) and pore volume of the catalysts were determined by using the nitrogen adsorption isotherms in volumetric adsorption systems (Micrometrics 3flex surface characterization analyzer).

2.3 Catalytic test

Catalytic reactions were carried out in a glass reactor equipped with an oil bath, magnetic stirrer, and reflux condenser. Typically, the reactor was charged with a commercial alumina supported metal catalyst, aqueous H₂O₂, oleic acid followed by addition of a tertiary alcohol as solvent. The reaction mixture was heated and kept for a predetermined period of time. After the reaction, the solution was cool down to room temperature. The resultant solution then underwent a derivatization process prior to be analysed by gas chromatography–mass spectrometry (GC–MS).

2.4 Quantitative Analysis of the Product

GC–MS was used for separation and quantification of methyl esters of fatty acids. Due to the adsorption problem on the stationary phase in GC columns, the reaction products were esterified to fatty acid methyl ester (FAME) before being analysed. The FAME was prepared according to Ichihara's method (Ichihara and

Fukubayashi, 2010). Firstly, 0.5 ml of reaction product was added into a gas-capped glass tube. Then, 0.3 ml HCl (9%w/w solution in methanol) and 1.5 ml of methanol were added. The solution was heated to 80°C and kept at this temperature for 2 hours, followed by cooling down to room temperature. The esterified products were extracted by adding 1 ml of hexane and 1 ml of deionized water to separate the organic phase and aqueous phase. Finally, the sample was dehydrated by sodium sulfate. The organic phase was injected into the GC–MS instrument. The GC/MS shimadzu QP2020 was equipped with HP-INNOWAX column (30m x 0.25 mm x 0.25 µm). Helium was used as a carrier gas with the flow rate of 30 ml/min. The injector split ratio was fixed at 10:1. The oven temperature program consisted of maintaining at 50°C for 1 min, then a ramp rate of 5°C/min to 150°C following by a hold-up time of 1 min, and then increased of the rate of 5°C/min to 260°C and held for 5 minutes. NIST14 data library was used to analyze data.

2.5 Calculation

It should be noted that the data in the results were plotted in relative value, due to term and condition of the collaborated company, which obtained from equation 1-4.

$$\%Conversion = \frac{\text{mole of oleic acid consumed}}{\text{mole of oleic acid before reaction}} \times 100 \quad (1)$$

$$\%Selectivity_A = \frac{\text{mole of product A}}{\text{mole of oleic acid consumed}} \times 100 \quad (2)$$

$$\%Yield_A = \frac{\%Conversion \times \%Selectivity_A}{100} \quad (3)$$

$$\text{Relative percentage} = \frac{\%Conversion \text{ or } \%Yield_A}{A \text{ numeric constant}} \quad (4)$$

3. Results and Discussion

The products obtained from oxidative cleavage of oleic acid in this research are consisted of SCFAs, MCFAs, aldehydes, dicarboxylic acids, and n-oxo carboxylic acids which are shown in Table 1.

3.1 Effect of catalyst loading

The effect of catalyst loading on oxidative cleavage of oleic acid using commercial metal catalysts supported on alumina was studied at loading of 1% and 10%. The results in Figure 2 and Figure 3 show that increasing catalyst loading of 1% to 10% resulted in the increase in yield of pelargonic acid (PA) and azelaic acid (AA) regardless of the fact that the overall conversion is

decreased. This can be anticipated from decreased in surface area of the high-loading catalysts, as shown in Table 2. The higher yields from 10% loading catalyst were obtained from the presence of higher content of active metal in the catalyst structure.

Table 1. Summary products from oxidative cleavage of oleic acid

Functional group	IUPAC name
Monocarboxylic acids	Hexanoic acid
	Heptanoic acid
	Octanoic acid
	Nonanoic acid
	Decanoic acid
Aldehydes	Hexanal
	Heptanal
	Octanal
	Nonanal
	Decanal
Dicarboxylic acids	Octanedioic acid
	Nonanedioic acid
n-oxo,carboxylic acid	8-Oxo-octanoic acid
	9-Oxononanoic acid

3.2 Effect of hydrogen peroxide-to-oleic acid ratio

The effect of hydrogen peroxide-to-oleic acid molar ratio were studied at oxidative cleavage of oleic acid using commercial metal catalysts supported on alumina at loading of 1% and 10%. Results in Figure 2 and Figure 3 show that the increase in hydrogen peroxide-to-oleic acid molar ratio from 1:1 to 10:1 result in increasing oleic acid conversion and increasing yield of PA and AA. It is suggested that the additional amount of hydrogen peroxide shifts the reaction equilibrium to form more products.

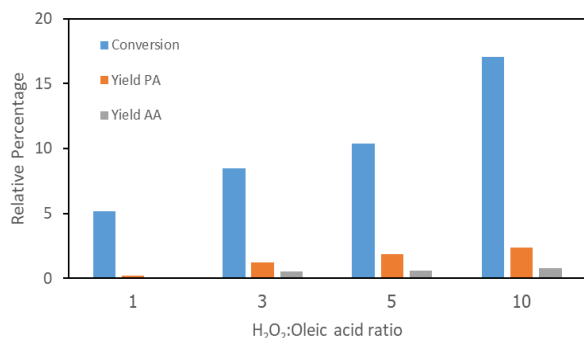


Figure 2. Effect of hydrogen peroxide-to-oleic acid ratio on the oxidative cleavage using 1% loading catalyst

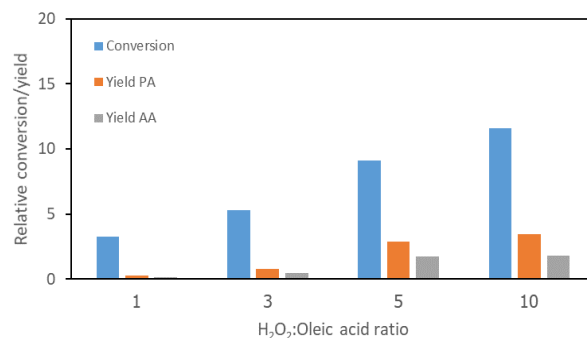


Figure 3. Effect of hydrogen peroxide-to-oleic acid ratio on the oxidative cleavage using 10% loading catalyst

Table 2. N₂-adsorption/desorption isotherms results.

%Catalyst loading	S _{BET} (m ² /g)	Pore volume (cm ³ /g)
1	290.26	0.568
10	269.50	0.494

3.3 Effect of reaction time

The oxidative cleavage of oleic acid using 10% loading catalyst in a batch reactor was monitored to study the effect of reaction time. The results show that the oleic acid conversion increases significantly within the first 30 minutes. The rate of the reaction slows down after 90 minutes. The yields of PA and AA increase progressively at the start until the reaction time of 120 minutes, after which they declined. This could be anticipated from the decomposed of H₂O₂ since the yields of aldehyde products dramatically increase at prolonged reaction time (see Figure 5).

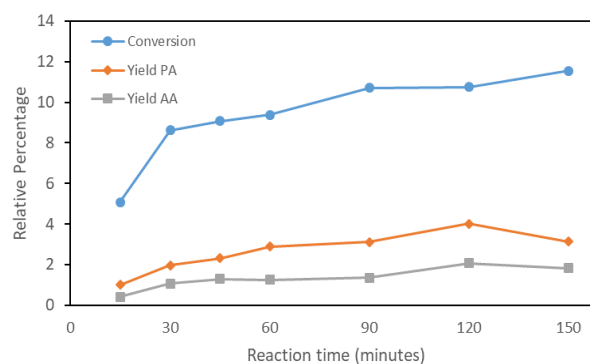


Figure 4. Effect of reaction time on the oxidative cleavage using 10% loading catalyst (Experimental condition: hydrogen peroxide-to-oleic acid ratio of 10/1)

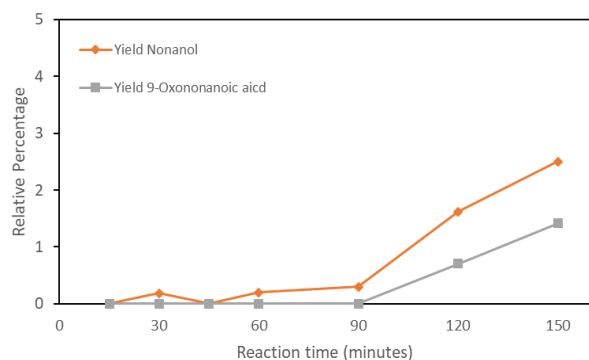


Figure 5. Increasing of aldehyde products with reaction time (Experimental condition: hydrogen peroxide-to-oleic acid ratio of 10/1)

4. Conclusions

SCFAs, MCFAs, dicarboxylic acid, and aldehyde products were found as products from oxidative cleavage of oleic acid using commercial catalysts supported on alumina. Oxidative cleavage of oleic acid on 10% loading catalyst with H₂O₂-to-oleic acid molar ratio of 10:1, resulted the highest PA and AA yield. It might be concluded that higher catalyst loading, and hydrogen peroxide-to-oleic acid molar ratio could improve acid products yield for the reaction between oleic acid and hydrogen peroxide.

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