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MICROWAVE FACILITATED THE SYNTHESIS OF ISOPROPYL MYRISTATE AND PALMITATE USING HETEROGENEOUS CATALYST

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ABSTRACT

In the present research, a microwave-intensified esterification reaction of myristic acid and palmitic acid with isopropyl alcohol (IPA) to produce an emollient ester using Amberlyst46 as a catalyst was studied. The effect of the ratio of molar fatty acid to alcohol, catalyst weight, reaction time, and microwave power on isopropyl myristate (IPM) and isopropyl palmitate (IPP) conversion and yield were investigated systematically. The results showed that catalyst weight and microwave power significantly affect the conversion and yield of IPM and IPP, respectively. The maximum conversion and yield of IPM were achieved under microwave irradiation power of 100% and catalyst weight of 15 wt.% while only 50% microwave power was required to achieve maximum conversion and yield of IPP using 18 wt.% of catalyst weight. These findings show that microwave-facilitated esterification reaction is a promising alternative method to produce emollient ester as the maximum conversion could achieve in a short reaction time.

Keywords: Esterification, Emollients, Microwave Irradiation, Amberlyst-46.

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INTRODUCTION

IPM and IPP are emollient esters that are extensively used in cosmetic and pharmaceutical products due to their characteristics and properties. These esters are non-toxic, can restore skin moisture and oil level, have good dispersibility, biodegradable, can act as excellent solvents in cosmetic formulations, and have a dry and mild taste.[1,2] IPM and IPP can be used as skin penetration enhancers in pharmaceutical products and are excellent solvents for mineral oils, lanolin, and silicones. The market value of emollient ester is US$ 174.8 million in 2022 and is projected to have growth of 3.1% during 2021–2026 calculated as a cumulative annual growth rate (CAGR). Today, most industries were used acids, bases, or metal oxides as catalysts for esterification which usually occur at high temperatures (120 - 230°C).[1,3] Despite high temperatures could remove water during the reaction, it can increase production costs and energy consumption.[1] Furthermore, the chemical esterification process results in a low-quality product that contains by-products that are aggressive to the skin and may pose a risk to human health. Extensive refining steps are required to avoid this problem, thereby increasing production costs.[4] Acid heterogeneous catalysts are proposed to overcome the problems caused by the use of such homogeneous catalysts.[5] The heterogeneous catalysts have some advantages such as high selectivity, no environmental pollution, low equipment corrosion, and ease of separation.[6] However, it requires longer reaction time due to mass transfer limitation caused by different phases.[7] Hence, the search for new methods that can produce IPM and IPP in a short time without producing waste has been emerging currently. The use of microwaves to facilitate chemical reactions has been developed and has proven could accelerate reactions.[8,9] Several studies have proven that the presence of microwave radiation causes collisions between molecules of compounds to become faster to form new compounds with a high level of purity.[10,11] The use of microwaves in accelerating this reaction has also been categorized as green chemistry because of the small amount of waste produced and the rapid formation of the desired product.[12-14] Oleochemical derivative products such as fatty acid methyl esters can be obtained in just 3 minutes with a yield of 98% from the transesterification/ esterification reaction of waste cooking oil with

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sodium methoxide catalyst.[15] This result is very fast compared to the usual transesterification reaction which takes 30 minutes.[16,17] Furthermore, the manufacture of fatty acid methyl esters can also be carried out directly from jatropha seeds in just 5 minutes using a heterogeneous strontium oxide catalyst.[18] In the present work, Amberlyst-46, a cation exchange resin, was used as a heterogeneous catalyst in microwave facilitated the esterification of isopropyl alcohol (IPA) with myristate and palmitic acid. The reaction parameters of the ratio of molar fatty acid to isopropyl alcohol, catalyst weight, reaction time, and microwave power were systematically investigated in triplicate to obtain a maximum IPM or IPP.

EXPERIMENTAL

Material and Methods

Isopropyl alcohol, myristic acid, palmitic acid, and others chemicals were purchased from a local chemical dealer and were used as received.

Esterification of Fatty Acids with Isopropyl Alcohol

The esterification of fatty acids with IPA using amberlyst-46 was conducted in the modified household microwave which was equipped with a condenser and magnetic stirring. Different molar ratios of fatty acids to IPA (1:1 to 1:5), catalyst weight of 6 to 21 wt.% with increments of 3 wt.%, reaction time of 10, 20, 30, 40, 50, and 75 minutes and microwave power (10, 30, 50, 70 and 100% based on 900-watt power output) were studied to examine the maximum IPP or IPM conversion. A 10 g of either myristic or palmitic acid and molecular sieve was mixed with an investigated volume of IPA and mass of the catalyst in 100 mL of the round-bottom flask. The mixture was irradiated based on investigated microwave power and reaction time. The IPP or IPM product was then separated from the catalyst and molecular sieve while the leftover IPA was vaporized until the constant weight of the product was obtained. The conversion of the ester was examined by measuring the acid number of fatty acids and the product (Eq.-1). The acid number was determined using the titrimetric method as described elsewhere.[19] Furthermore the FT-IR and GC-MS analysis were used to verify the formation of the ester products.

$$The\ Conversion = \frac{Acid_{FA} - Acid_{Ester}}{Acid_{FA}}\ x\ 100 \qquad (1)$$

Statistical Analysis

All the experiments were conducted three times to decrease an error. The statistical significance effect of each parameter was evaluated by one-way ANOVA (significance level set to $\alpha = 0.05$) followed by Tukey's test to compare the results mean using Statistical v13.6 software.

RESULTS AND DISCUSSION

Effect of Molar Ratio of Fatty Acid to Isopropyl Alcohol

Stoichiometrically, a 1:1 ratio molar of fatty acid to IPA is required to complete the esterification reaction. However, an excess of IPA is used to drive the equilibrium towards the product side.[20,21] Therefore the effect of ratio molar in the esterification of fatty acids with IPA under microwave irradiation using Amberlyst-46 was investigated at five different ratios of 1:1 to 1:5 in the increment of 1 molar. As shown in Fig.-1A, for a given of ratio molar, the conversion of either IPP or IPM increased gradually with the increase of ratio molar. The IPM conversion of 45.7 ± 3.1% at a ratio molar of 1:1 was increased and reached a maximum of 66.2 ± 1.8% at a ratio molar of 1:3 and the conversion began to decrease when the ratio molar was further increased to 1:4 and 1:5. The similar pattern also observed in IPP with the maximum conversion of 63.9 ± 1.6% obtained at ratio molar 1:3. This presumably due to increasing methanol volume beyond the peak could trigger the reversible esterification reaction back to the reactants.[5] This result is in agreement with previous results which reported the decreasing fatty acid methyl ester conversion in an excess of methanol amount after it reached the maximum conversion.[22,23] In contrast, the highest IPM yield (68.1 ± 3.8%) was obtained at a ratio molar of 1:4 and was decreased in the addition of methanol amount as shown in Fig.- 2A. The IPP yield has a similar line graph pattern to the conversion graph and was observed as a maximum yield of 61.8 ± 2.7% at a ratio molar of 1:3. Furthermore the ANOVA result indicated that the ratio molar of fatty acids to IPA has a significant effect on both conversion and yield of IPM and IPP. The significant effect on IPM is mainly driven by the low

and high conversion at ratios of 1:1 and 1:3, respectively, while all ratios molar tested significantly affect the conversion of IPP.

Effect of Catalyst Weight

To study the effect of catalyst weight on IPM and IPP conversion and yield, various Amberlyst-46 concentrations ranging from 6 to 21 wt.% with an increment of 3 wt.% were used to catalyze the esterification reaction. The reaction condition to examine this parameter was a ratio molar of 1:3, a reaction time of 30 minutes, and 50% of microwave power. The IPM conversion increased gradually from 58.7 ± 1.0% at a catalyst weight of 6 wt.% to 66.2 ± 1.8% at 15 wt.% of catalyst (Fig.-1B). However, the IPM conversion decreased slightly with the increase in catalyst weight. Similarly, increasing catalyst weight from 6 to 15 wt.% only recorded a marginal effect on the IPP conversion. Increasing the Amberlyst-46 weight above 15 wt.% resulted in a clear decline in IPP conversion. As shown in Fig.-2B the IPP yields were substantially increased when the Amberlyst-46 concentration increased from 6 wt.% to 18 wt.% and a further increase in catalyst weight reduced the yield. The maximum IPP yield of 80.4 ± 3.9 was observed at a catalyst weight of 18 wt.%. In contrast, the increasing catalyst weight did not affect the IPM yield. The IPM yield tends to slightly decrease at catalyst weights of 9 and 12 wt.%. The maximum IPM yield of 60.5 ± 5.5% occurred at a catalyst weight of 6 wt.%. This result is similar to other published research which concluded that increasing bio-catalyst could increase the conversion of IPP.[24] Chandane, *et al.* [2017] confirmed a similar result in the synthesis of IPP using p-toluene sulfonic acid as a catalyst.[25] The statistical analysis of the variance test showed that catalyst weight has a significant effect on both IPM and IPP conversion and yield. Further, the Tukey test revealed that the significance was mainly driven by low and high conversion of IPM using a concentration of 6 and 15 wt.% while all the catalyst weights tested affected the IPP conversion.

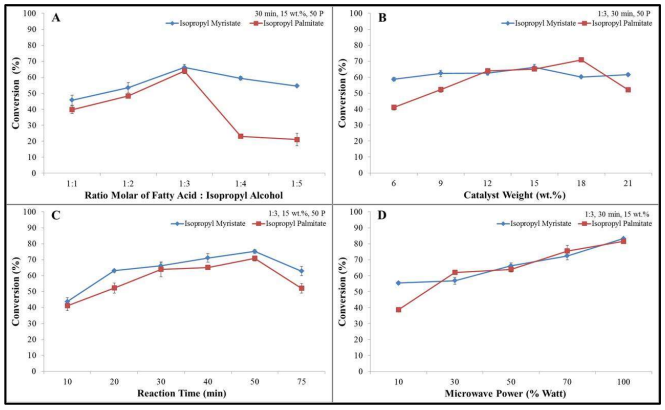

Fig.-1: The effect of (A) Ratio Molar of Fatty Acid to Isopropyl Alcohol; (B) Catalyst Weight; (C) Reaction Time; and (D) Microwave Power on IPP or IPM Conversion.

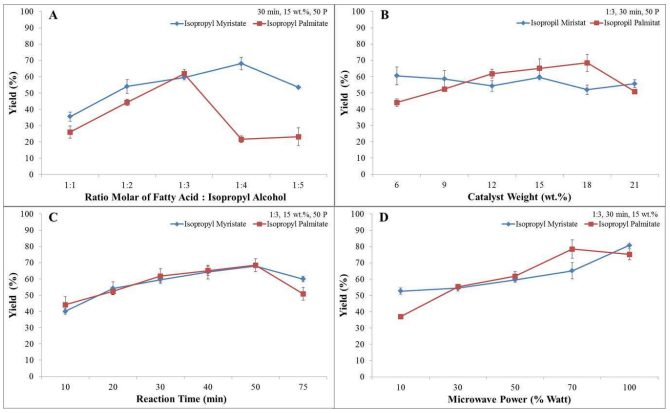

Fig.-2: The Effect of (A) Ratio Molar of Fatty Acid to Isopropyl Alcohol; (B) Catalyst Weight; (C) Reaction Time; and (D) Microwave Power on IPP or IPM Yield

Effect of Reaction Time

Reaction time could drive the efficiency of IPM and IPP formation and also the quality of final products.[26] To study the effect of reaction time on IPM and IPP conversion, the reaction time was varying from 10 to 75 min at 10 min and 25 min intervals were investigated at a ratio molar of fatty acids to IPA of 1:3, catalyst weight of 15%, and 50% microwave power. As expected the conversion rate increases with reaction time. Frequently the reaction rate was low due to the mixing and dispersion of IPA onto the fatty acid being relatively low. The reaction proceeds faster with increasing time until the maximum yield is reached. As shown in figure 1C, at a reaction time of 10 min the IPM conversion was obtained as 43.7 ± 2.5% and it was observed to increase to 75.2 ± 1.1% at a reaction time of 50 min before decreasing to 62.9 ± 2.8 at 75 min. The IPP conversion also increased gradually in the increase of reaction time to reach the maximum conversion of 70.9 ± 1.1 at a reaction time of 50 min. Likewise, both IPM and IPP yields constantly increased to achieve a maximum yield of 67.9 ± 0.7% and 68.5 ± 5.2%, respectively, at a reaction time of 50 min. Fu, *et al.* [2015] reported a similar result that the conversion of IPP was raised in prolonged reaction time.[27] A one-way ANOVA established a significant effect of the reaction time on the IPM and IPP conversion which is mainly driven by the low and high conversion of IPM at a reaction time of 10 and 50 min while all the reaction times significantly affect the IPP conversion.

Effect of Microwave Power

It has been proved that microwaves could accelerate chemical reactions.[28,29] Microwave induces molecular rotation arising from dipole alignment with the external. Generally, the higher the microwave power, the faster the dipole reorientated under the microwave.[30] Therefore, The influence of microwave power on both IPM and IPP conversion and yield at the ratio molar of 1:3, the reaction time of 30 min, and catalyst weight of 15 wt.% were demonstrated in figure 1D and 2D. The enhancement of microwave power from 10% to 100% resulted in an increase in both conversion and yield under the present conditions. The maximum conversion of 83.3 ± 0.1% and 81.5 ± 1.4% for IPM and IPP, respectively, was achieved using microwave power of 100%. In contrast, the maximum yield of IPP was obtained under irradiation of 70% microwave power while the highest IPM yield was observed using 100% power. This result is similar to the published result in the transesterification of chicken feather meal oil using a catalyst derived from chicken eggshell which concluded that microwave power affects the conversion of fatty acid methyl ester.[29] Furthermore, a significant effect was observed in microwave power on both IPM and IPP conversions and yields. The significance effect determined by ANOVA obtained for IPM and IPP conversions is driven by all powers used.

CONCLUSION

In this study, microwave irradiation to the accelerated chemical reaction was investigated for the esterification reaction. The proposed process proved to be greener and is an alternative method to produce IPM and IPP. The maximum conversion and yield of IPM were 83.3 ± 0.1% and 80.7 ± 0.6%, respectively, achieved under reaction condition of a ratio of molar myristic acid to IPA of 1:3, the reaction time of 30 min, catalyst weight of 15 wt.% and microwave power of 100% while the maximum conversion and yield of IPP of 83.7 ± 1.7 and 80.4 ± 3.9% were achieved under 50% microwave power and catalyst weight of 18 wt.%. The modified microwave apparatus intensified the esterification of IPM and IPP could be considered technically feasible for actual deployment at the small-scale processing units.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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