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Esterification of malic acid on various catalysts

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Objectives. *The study aims to identify the optimal choice of an effective catalyst for the esterification of malic acid to produce esters of high purity.*
Methods. *To determine the qualitative and quantitative composition of reaction masses, the following analysis methods were used: mass spectroscopy (using FinniganTrace DSQ device with NIST 2002, Xcalibur 1.31 Sp 5 database) and gas–liquid chromatography (using the Kristall 2000M software and hardware complex).*
Results. *Esters of malic acid and butyl alcohol of normal structure were synthesized using the following catalysts: sulfuric, orthophosphoric, p-toluenesulfonic acid, Amberlyst 36 Dry, Amberlyst 36 Wet, KU-2-FPP, and KIF-T. The obtained products were analyzed by gas–liquid chromatography. The structure of the products was confirmed by mass spectrometry. Schemes for the formation of byproducts are proposed. The yields and purity of the malic acid butyl esters obtained using different catalysts were evaluated. The results show that the heterogeneous catalyst Amberlyst 36 Dry is optimal for obtaining a pure malic acid ester with a maximum yield.*
Conclusions. *The results show that during the esterification of malic acid with butyl alcohol of normal structure, byproducts, such as esters of fumaric and maleic acids, are formed using different catalysts. An accumulation of byproducts occurs as a result of reactions of dehydration of malic acid or its ester. The results also show that the number of byproducts is almost independent of the catalyst, with the exception of sulfuric acid. The Amberlyst 36 Dry catalyst provides an optimal ratio between conversion and selectivity for malic acid dibutyl ester production.*

Keywords: *esterification, esters, malic acid, n-butanol, Amberlyst 36 Dry.*

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Этерификация яблочной кислоты на различных катализаторах

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Цели. *Обосновать выбор эффективного катализатора этерификации яблочной кислоты для получения сложных эфиров высокой степени чистоты.*
Методы. *Для определения качественного и количественного состава реакционных масс были использованы следующие методы анализа: масс-спектроскопия (на приборе FinniganTrace DSQ с базой NIST 2002, Xcalibur 1.31. Sp 5) и газожидкостная хроматография (на аппаратно-программном комплексе «Кристалл 2000М»).*
Результаты. *Синтезированы сложные эфиры яблочной кислоты и бутилового спирта нормального строения на следующих катализаторах: серная, ортофосфорная, n-толуолсульфокислота, Amberlyst 36 Dry, Amberlyst 36 Wet, КУ-2-ФПП и КИФ-Т. Полученные продукты проанализированы методом газожидкостной хроматографии. Строение продуктов подтверждено масс-спектрометрическим методом. Предложены схемы образования побочных продуктов. Оценены выходы и чистота бутилового эфира яблочной кислоты, полученного на разных катализаторах. Показано, что для получения чистого сложного эфира яблочной кислоты с максимальным выходом оптимальным является гетерогенный катализатор Amberlyst 36 Dry.*
Выводы. *Установлено, что при этерификации яблочной кислоты бутиловым спиртом нормального строения на разных катализаторах образуются побочные продукты – сложные эфиры фумаровой и малеиновой кислот. Накопление побочных продуктов происходит в результате реакций дегидратации яблочной кислоты или его сложного эфира. Показано, что количество побочных продуктов практически не зависит от катализатора, за исключением серной кислоты. Для получения дибутилового эфира яблочной кислоты рекомендуется использовать сульфокатионит Amberlyst 36 Dry, обеспечивающий оптимальное соотношение между конверсией и селективностью.*

Ключевые слова: *этерификация, сложные эфиры, яблочная кислота, н-бутанол, Amberlyst 36 Dry.*

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INTRODUCTION

Modern trends within the chemical industry have been aimed at finding processes that are independent from oil and petroleum products. Great interest is shown in materials obtained from renewable sources of raw materials [1], such as alcohols and carboxylic acids.

Today, esters are in high demand in the production of paints, plasticizers, copolymers, various additives to lubricants, and pharmaceuticals. Esters of hydroxycarboxylic acids obtained from renewable natural resources are of particular interest. For example, trisubstituted citric acid esters-trialkylcitrates, obtained by esterification of citric acid with aliphatic alcohols C_2 and C_4, are used as non-toxic plasticizers for PVC products or solvents in the production of food additives, children’s toys, and household packaging [2]. Plasticizers based on citric acid esters are environmentally friendly and have a high plasticizing ability. Another promising industrial product, completely obtained from plant components, is the ester of malic acid and *n*-butyl alcohol. Malic acid is a dibasic oxocarboxylic acid and is used as an additive in the food industry and in medicine. There are known methods for obtaining malic acid from vegetable raw materials, such as unripe apples, sea buckthorn, and cotton leaves as well as and from chemical methods, such as the catalytic hydration of maleic or fumaric acid, which are derived from maleic anhydride.

This process is catalyzed by fumarate hydratase or fumarase. Maleic anhydride, in turn, is obtained by the oxidation of hydrocarbons, primarily butane [3]. Fumaric acid can also be obtained from various enzymatic hydrolysates of cellulose-containing raw materials under the action of a biocatalyst [4]. *n*-Butyl alcohol is used in the paint industry as a solvent as well as in the production of resins, plasticizers, and many other organic compounds. It can be obtained from chemically raw materials or by processing sucrose, starch, or cellulose from agricultural crops [5].

The simplest method for producing esters is direct esterification of acids with alcohols in the presence of a catalyst [6]. Esterification of dicarboxylic acids with alcohols can be performed without a catalyst; however, the reaction proceeds slowly, and high temperatures (200–300°C) are required to achieve sufficient speed [7]. For the esterification of dicarboxylic acids, a process involving mineral acids (sulfuric, hydrochloric, orthophosphoric, boric), alkylsulfonic acids (benzene or *p*-toluene sulfonic acids) and arylsulfochloride as catalysts are used [8−10]. Further, organic titanium compounds are also highly active [11], and recently, heterogeneous catalysts have been used in the production of esters [12–14].

In industrial applications, the liquid phase method of esterification is widely used in periodic- or continuous-motion equipment. The main stages of the liquid phase method are esterification, neutralization of the reaction mass, washing from a homogeneous catalyst, and rectification [15]. However, in order to simplify the design of technology used to obtain esters, the use of heterogeneous catalysts simplifies the process by eliminating the stages of neutralization, washing, and drying, and it also helps to reduce the loss of organic acid. Additionally, heterogeneous catalysts are easily regenerated, allowing them to be used repeatedly. It is also important to reduce the number of generated byproducts, which will reduce energy consumption at the stage of rectification.

Several studies have researched the possibility of obtaining malic acid esters by esterification using homogeneous catalysts [16–18]; however, there are no data on the esterification of malic acid using heterogeneous catalysts. Thus, the aim of this work is to select an effective heterogeneous catalyst for the esterification of malic acid to produce esters of high purity.

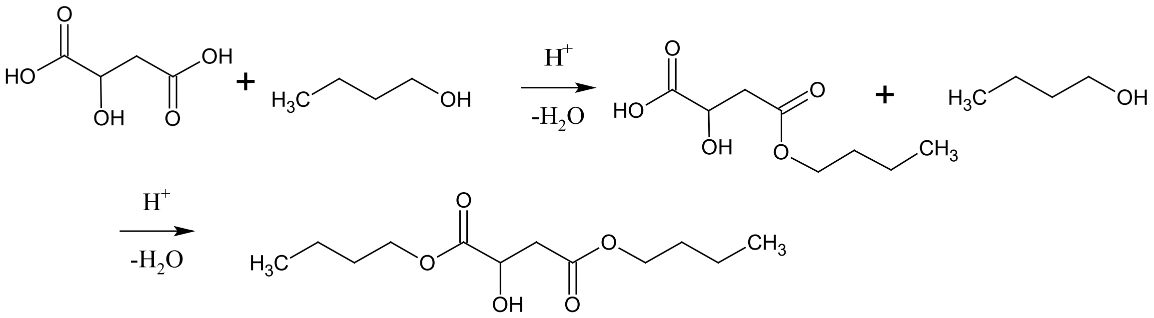
MATERIALS AND METHODS

To synthesize esters, racemic DL-malic acid was used with a base substance concentration of at least 99.3%, along with CP grade *n*-butyl alcohol with a purity of at least 99.8%. AR grade benzene was used as an azeotroping agent. As catalysts, this experiment used concentrated sulfuric acid (98% solution), CP grade orthophosphoric acid with a purity of at least 85%, pure grade *p*-toluenesulfonic acid, KU-2 FPP, KIF-T, and sulfocationic catalysts Amberlyst 36 Dry and Amberlyst 36 Wet.

Before synthesis, *p*-toluenesulfonic acid was purified in a similar method as in [19]. The catalysts KU-2 FPP (moisture content no more than 30%) and KIF-T (moisture content no more than 30–60%) were crushed to the size of 1–2 mm and used without additional drying. Amberlyst 36 Dry (water content no more than from 1.5 to 2%) and Amberlyst 36 Wet (moisture content no more than 53−59%) were also used without additional drying.

Esterification of *n*-butyl alcohol with malic acid proceeded according to the scheme in Reaction 1.

A 250 ml round-bottom flask equipped with a Din–Stark trap and a Liebig condenser was filled with 10 g (0.07 mol) of malic acid, 4× molar excess volume of alcohol (22 ml of *n*-buthanol), 40 ml of benzene, and 1 wt % of the tested catalyst. The resulting mixture was boiled with azeotropic distillation of water until the reaction ended. When using a homogeneous catalyst, the reaction mixture was first washed with a solution of sodium bicarbonate to neutralize the acid, then with distilled water to a neutral pH. When using a heterogeneous catalyst, it was filtered. The resulting reaction mass was distilled at a residual pressure



Reaction 1

of 50 mm Hg for separation of benzene and excess butyl alcohol. Pure ester was extracted by fractional distillation at a residual pressure of 13−15 mmHg. The boiling point of dibutyl ester of malic acid is 185−186°C.

RESULTS AND DISCUSSION

The analysis of the reaction mass and the obtained esters was performed using gas–liquid chromatography on the Chromatec Analytic Kristall-2000M chromatograph, equipped with a flame ionization detector and a capillary column with a grafted non-polar phase DB-1, 100 m × 0.2 mm × 0.5 µm. The analysis parameters were as follows:

1) The column temperature was 150°C during the first 20 min, then the column temperature rose up to 260°C with a heating rate of 5°C per minute.
2) The injector temperature was 250°C.
3) The detector temperature was 280°C.
4) The carrier gas was helium, split ratio 1/40.

The sample volume is 1 µl.

A typical chromatogram of malic acid dibutyl ester is shown in Fig. 1.

The chromatogram clearly shows two peaks next to the main product. To identify these peaks, an analysis was conducted using a Finnigan Trace DSQ mass spectrometer via electron impact ionization, set at 70 eV, using the National Institute of Standards and Technology (NIST) 2002, Xcalibur 1.31 Sp 5 database[1]. During the analysis, a 30 m long ZB 5MS capillary column with a weak polar phase and an inner diameter of 0.32 mm was used. The injector temperature was set at 250°C, and the transfer line temperature was set at 280°C. The column temperature was initially 80°C during the first 1 min, followed by a temperature elevation rate of 10°C/min until 300°C. The carrier gas was helium, set at a flow rate of 1.3 ml/min.

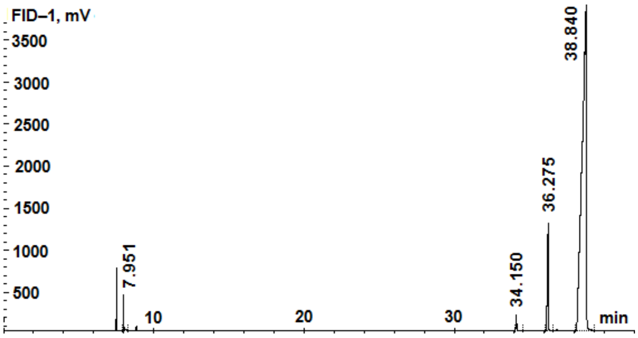


Fig. 1. Chromatogram of malic acid dibutyl ester.

According to the NIST database, the peak at 34 min was attributed to the maleic acid dibutyl ester (Fig. 2), the peak at 36 min was attributed to the fumaric acid dibutyl ester (Fig. 3), and the main peak at 38 min was attributed to the malic acid butyl ester (Fig. 4).

The formation of maleic and fumaric acid esters is possible by two means. The first option is the esterification of the corresponding unsaturated acids contained as impurities in malic acid, by butanol, as represented in Reaction 2.

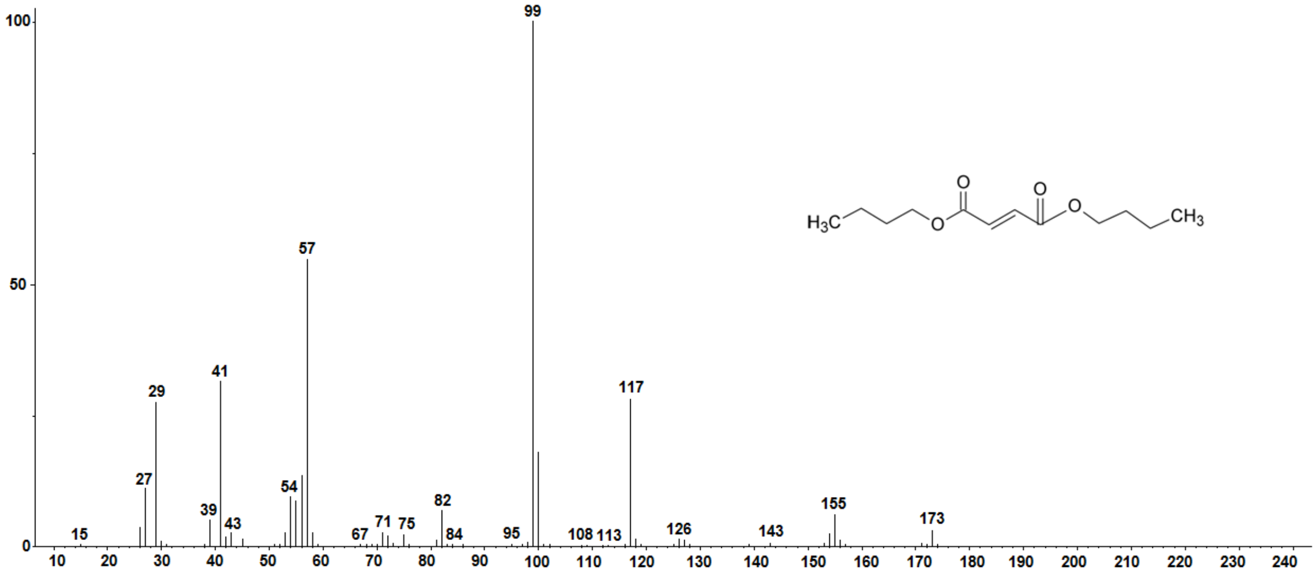


Fig. 2. Mass spectrum of maleic acid dibutyl ester.

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[1] NIST Chemistry Webbook, SRD 69. Available from: webbook.nist.gov/chemistry/ (Accessed September 20, 2017). https://doi.org/10.18434/T4D303

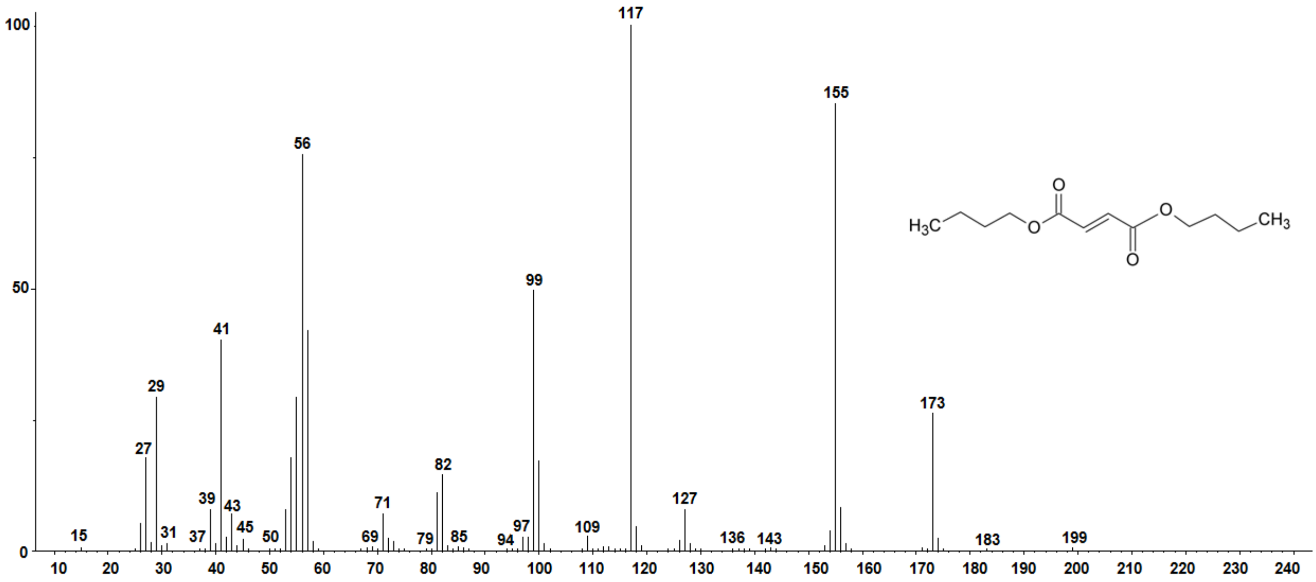


Fig. 3. Mass spectrum of fumaric acid dibutyl ester.

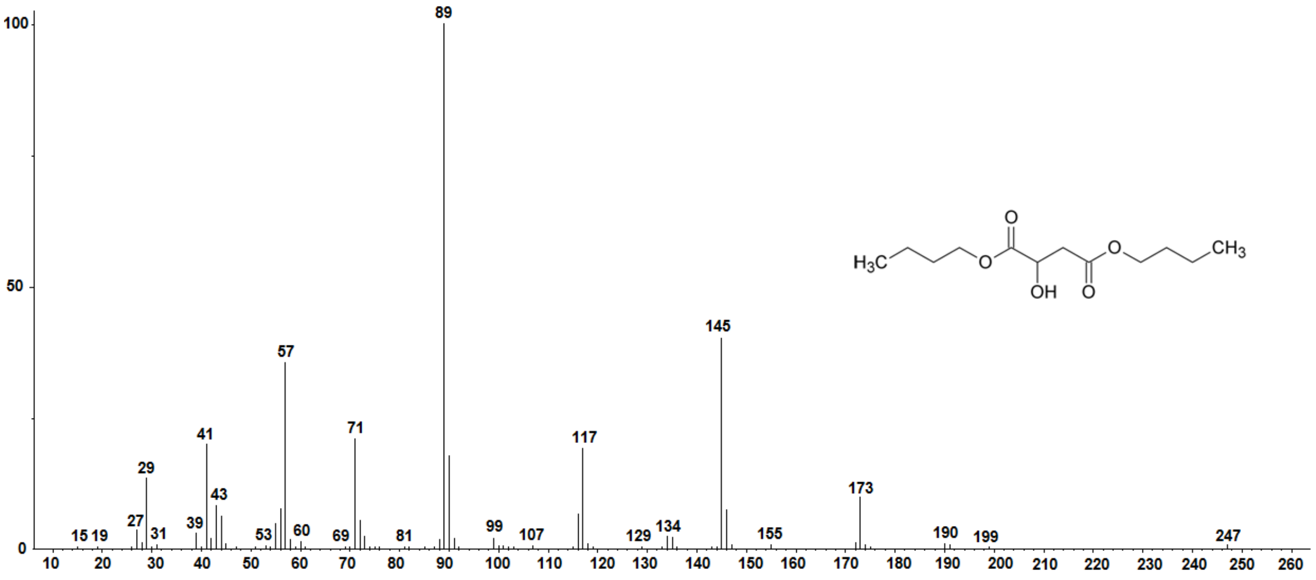
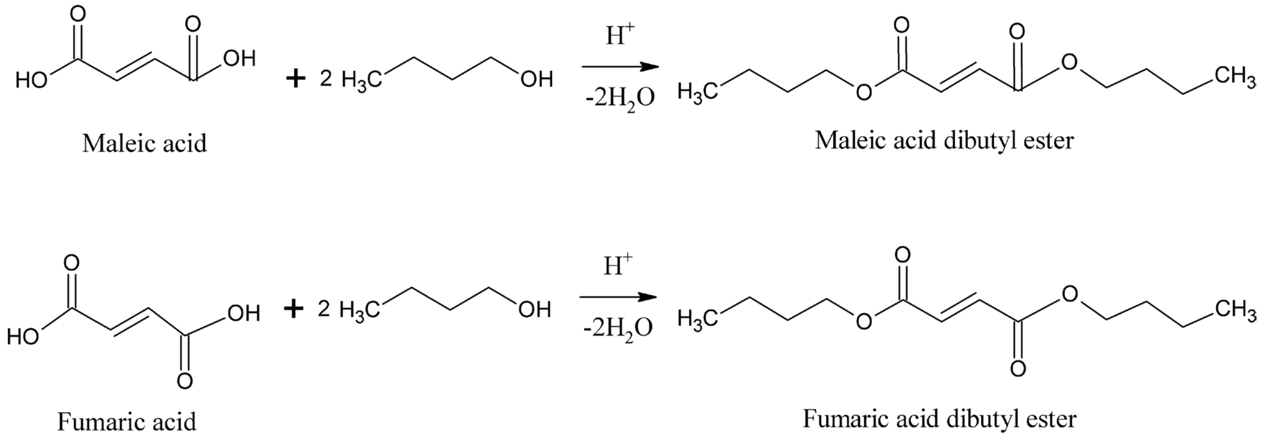


Fig. 4. Mass spectrum of malic acid dibutyl ester.



Reaction 2

At the same time, the content of maleic acid dibutyl ester should be significantly higher since this acid is the main impurity in the initial material.

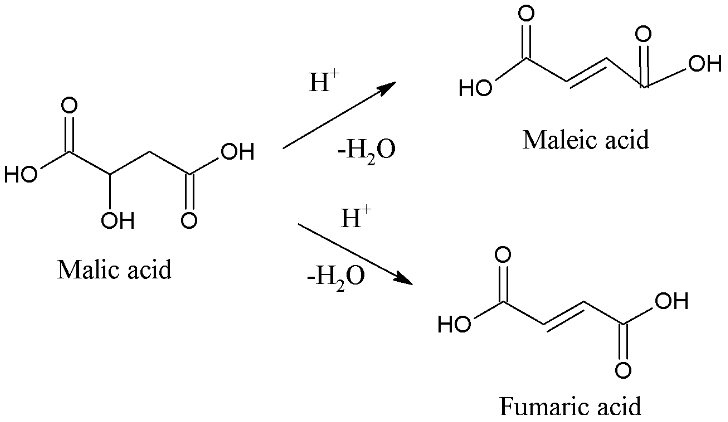
The second option is either the dehydration of malic acid followed by esterification, as shown in Reactions 3 and 2, respectively, or dehydration of the malic acid esters themselves, as shown in Reaction 4. The more likely product in this case is fumaric acid ester.

The yields of butyl ester of malic acid were as follows: 71% for sulfuric acid, 68% for orthophosphoric acid, 56% for *p*-toluenesulfonic acid, 70% for Amberlyst 36 Dry, and 86% for KU-2 FPP. When using the Amberlyst 36 Wet and KIF-T catalysts, the reaction mass was tarred during the synthesis process, so that it was not possible to obtain a pure ester when using these catalysts. Impurities of maleic and fumaric acid esters were present in all the samples and were obtained in different amounts. The amount of maleic acid esters exceeded the content of fumaric acid esters, indicating that their formation occurred in the second option.

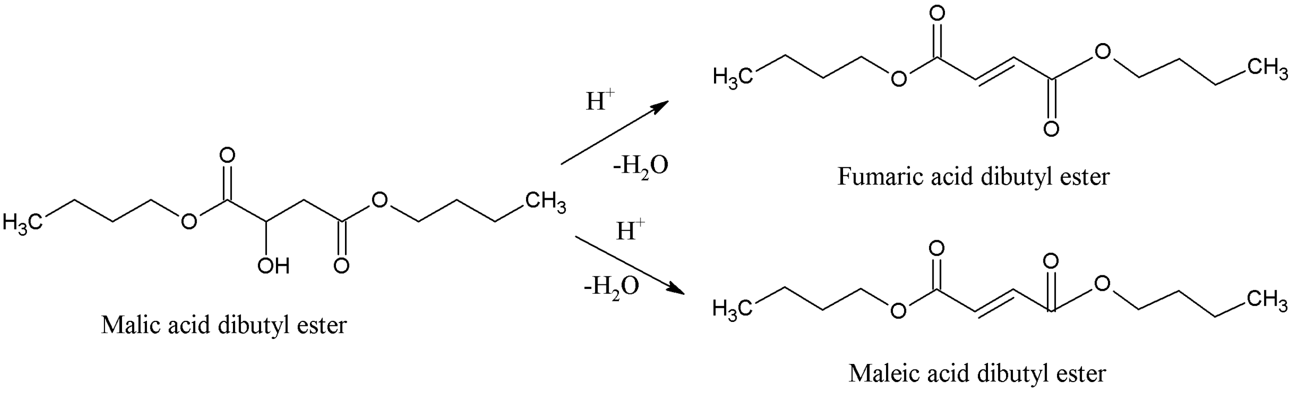
To assess the activity of the studied catalysts, several experiments were conducted under identical initial conditions; the temperature was set at 85°C, the amount of catalyst was 1 wt %, and the synthesis time was 80 min. The reaction mass was analyzed, and the conversion of malic acid was calculated. The composition of the final products was also analyzed after isolation and purification, according to the method described above. The results are given in the table.

The results show that the conversion of malic acid, as expected, is maximal on sulfuric acid. The conversion on Amberlyst 36 Dry is comparable to the conversion on p-toluenesulfonic acid. The decrease in malic acid conversion when using Amberlyst 36 Wet is due to the smaller number of active centers than Amberlyst 36 Dry (a limitation of the water content in the catalyst). Orthophosphoric acid, KU-2 FPP, and KIF-T had the least catalytic activity in the reaction of malic acid esterification during the considered time period.

When the finished products were isolated, the content of byproducts did not change significantly. The table shows that using sulfuric acid as a catalyst yields the highest percentage of impurities. When using the other catalysts, except for Amberlyst 36 Wet and KIF-T, the concentration of maleic and fumaric acid esters is approximately the same level and is



Reaction 3



Reaction 4

Analysis of reaction mass and product on different catalysts

Catalyst	Conversion of malic acid at 80 minutes, %	Concentration of the product after purification, %		
		Byproducts	Fumaric acid dibutyl ester	Main product
Sulfuric acid	95.0	0.9	12.6	86.5
Orthophosphoric acid	15.9	0.05	1.15	98.8
p-Toluenesulfonic acid	45.4	0.2	1.1	98.7
Amberlyst 36 Dry	47.1	0.05	1.25	98.7
Amberlyst 36 Wet	30.8	Tarring of the reaction mass		
KU-2-FPP	14.3	0.06	1.24	98.7
KIF-T	5.98	Tarring of the reaction mass		

1.2–1.3 wt %. Regarding Amberlyst 36 Wet and KIF-T, the tarring of the reaction mass may be associated with higher catalytic activity in the dehydration reaction and possible oligomerization of unsaturated acids, although the main parameters, i.e., total static exchange capacity and surface area, of Amberlyst 36 Wet and Amberlyst 36 Dry are almost equal.

Overall, these results show that, among the catalysts tested in this study, Amberlyst 36 Dry yields higher conversion and selectivity in the malic acid esterification process.

CONCLUSIONS

The results of this study show that during the esterification of malic acid with butyl alcohol of normal structure, byproducts, such as esters of fumaric and maleic acids, are formed using different catalysts. The accumulation of byproducts occurs as a result of reactions of dehydration of malic acid or its ester. This study shows that the number of byproducts is almost independent of the catalyst, except for sulfuric acid. In order to obtain the dibutyl ester of malic acid, Amberlyst 36 Dry was shown provide an optimal ratio between conversion and selectivity.

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The authors declare no conflicts of interest.

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