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MICROWAVE ACTIVATION OF ADDITION OF 1-HEXENE AND BUTANOIC ACID REACTION

Abstract. The possibility of carrying out the synthesis reaction hexylbutanoate (flavor in the food and perfume industry) by butanoic acid joining 1-hexene in the presence of sulfuric acid under microwave irradiation is demonstrated. Optimum process conditions (microwave irradiation power, duration, and the ratio of the initial reactants catalyst) were determined. The product yield gradually increases with increasing irradiation power, with further increase of microwave power resinification reaction mass and a reduction in yield are observed. The optimal condition for the synthesis of a ratio of the starting reactants and catalyst [butanoic acid]: [1-hexene] [conc. H2SO4] = 1: 1: $1.7 \cdot 10^{-2}$, the microwave irradiation power = 600 W, the process time 6 min. The yield of the product under found conditions is 74.4%. The strongest impact on the course of the reaction has a power of microwave irradiation, the weakest influence has aratio of the starting reagents. The yield was determined by gas chromatography-mass spectrometry using a capillary column HP-FFAP 30 m and an inner diameter of 0.25 mm, consisting of nitroterephtalic acid modified polyethylene glycol. Our proposed method of obtaining hexylbutanoate, compared with the known methods can significantly reduce the duration of the process and consistent with the principles of green chemistry.
Keywords: microwave synthesis, hexylbutanoate, butanoic acid, 1-hexene, irradiation power.

1 Introduction

Carboxylic acid esters are widely used as practical medicines component, food essences and components of various perfumes [1,2]. Hexylbutanoate ester has a characteristic fruity odor similar to the smell of pineapple [3]. In nature, it can be found in the composition of fruits and berries, as part of the essential oils of lavender and lavandula [4]. It is used as a flavoring of food products (bakery products, ice cream, candy, soft drinks) and in the perfume industry [5].

Chemical synthesis under microwave irradiation (microwave radiation) is currently the fastest growing method of organic synthesis [6-10]. Application of microwave irradiation in the chemical synthesis depends on its ability to accelerate many chemical reactions to tens and hundreds of times and theability of rapid volumetric heating of the liquid and solid samples. This feature microwave irradiation consistent with the principles of "green chemistry" – the scientific direction in chemistry, which can be attributed any improvement of chemical processes, which has a positive effect on the environment [8]. Opportunities offered by using microwave radiation in chemistry, have aroused great interest in the study and uses of microwave exposure effects.

Known methods for the synthesis of carboxylic acid esters direct esterification reaction under microwave irradiation [6, 9-11]. In the present study, we investigated the addition reaction of 1-hexene to butyric acid in the presence of aconcentrated sulfuric acid catalyst under microwave irradiation.

$$CH_3CH_2CH_2C(=O)-OH + CH_3CH_2CH_2CH_2CH{=}CH_2 \xrightarrow[-H_2O]{H_2SO_4,\ h\nu} CH_3CH_2CH_2C(=O)-O-CH_2CH_2CH_2CH_2CH_2CH_3$$

Scheme 1. Synthesis of hexylbutanoate

2 Experimental

A series of experiments were conducted to obtain hexylbutanoate to determine the optimum conditions, i.e. irradiation power impact on the yield, process time, ratio of reactants and catalyst.

Reactive butanoic acid, 1-hexene and concentrated sulfuric acid were used without purification. The test was performed in the microwave.

The yield was determined by chromatography on a gas chromatography-mass spectrometer Agilent 7890A /5975C (USA).

Chromatographic conditions: mobile phase (carrier gas) - helium; evaporator temperature 210^{0}C, flow discharge (Split) 1000:1; column oven temperature onset 50^{0}C (1 min), the temperature rise of 5^{0}C per minute, the end of 200^{0}C, held at this temperature for 1 minute, the total analysis time 32 min; ionization mode of the mass by electron impact detector. Capillary chromatography column HP-FFAP, column length 30 m, internal diameter 0.25 mm, stationary phase - nitroterephthalic acid modified by polyethylene glycol. Hexylbutanoate retention time 8.8 minutes (Figure 1)

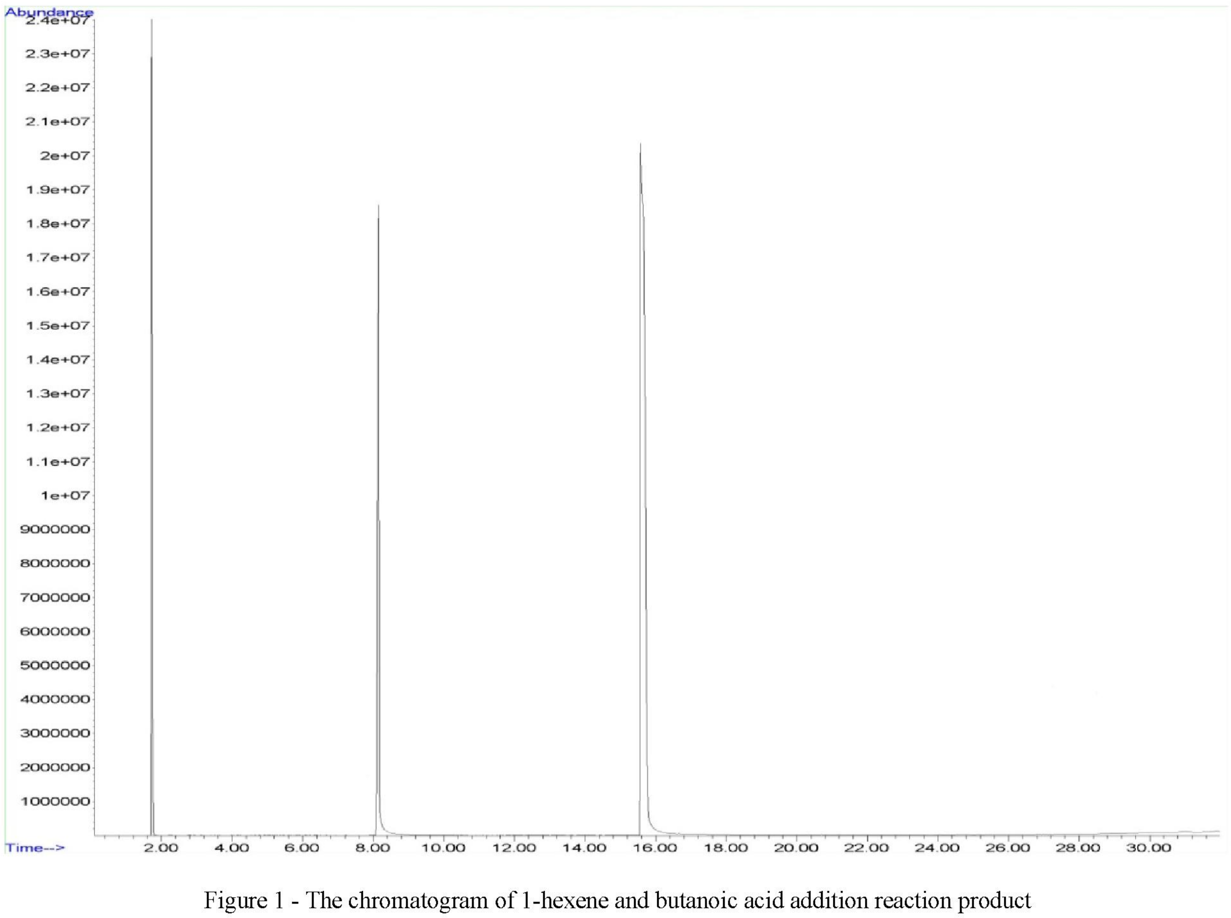

Figure 1 - The chromatogram of 1-hexene and butanoic acid addition reaction product

The reaction product – hexylbutanoate is identified by mass-selective detection, themass spectrum of the product is shown in Figure 2. Mass-fragments of hexylbutanoate are present in the mass spectrum, mass spectrum data is consistent with the data of NIST08 base.

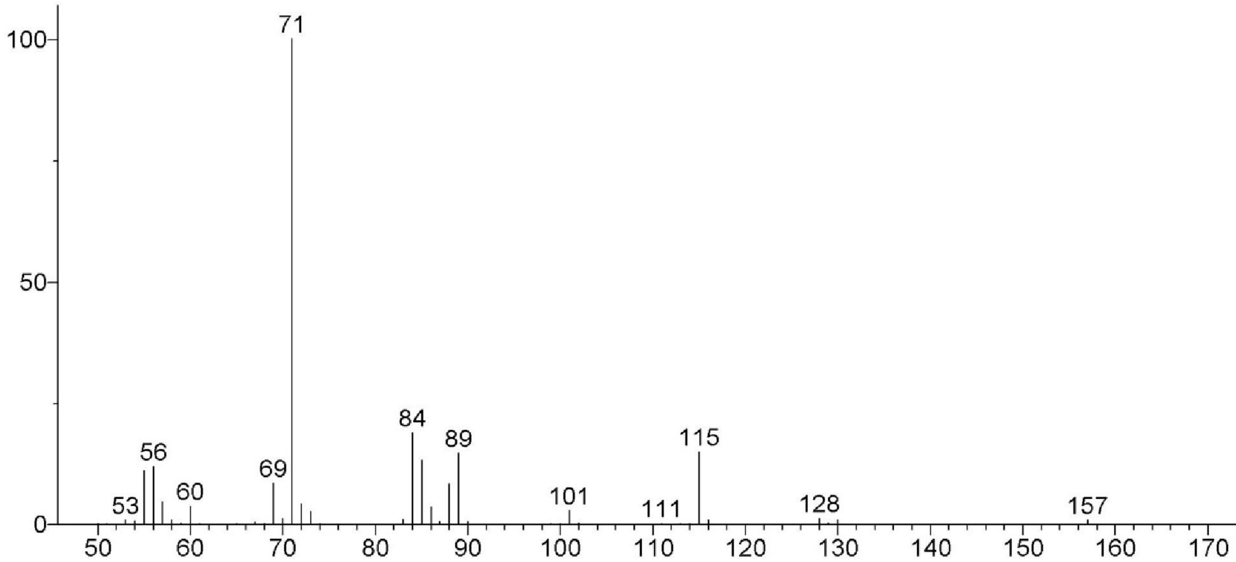

Figure 2 - The mass spectrum of hexylbutanoate obtained by the addition reaction of hexene and 1-butanoic acid

3 Results and discussion

Previously, it has been found that microwave radiation can be successfully used for the synthesis of esters of carboxylic acids with alcohols esterification reaction [6, 9-11].

The possibility of using microwave irradiation in the synthesis hexylbutanoate in the presence of sulfuric acid was presented. Table 1 shows the results of experiments for finding the optimal conditions of the addition reaction of 1-hexene to butyric acid.

Table 1 - Connection of 1-hexene and butanoic acid in the presence of sulfuric acid under microwave irradiation

№	The ratio of the reactants, mol			Reaction conditions		The yield,% (W)
	Butanoic acid	1-Hexene	Sulfuric acid	Power of microwave irradiation	Time, min	
1	1	1	$1{,}7\cdot10^{-2}$	100	3	4,2
2	1	1	$1{,}7\cdot10^{-2}$	180	3	9,3
3	1	1	$1{,}7\cdot10^{-2}$	300	3	18,6
4	1	1	$1{,}7\cdot10^{-2}$	450	3	24,1
5	1	1	$1{,}7\cdot10^{-2}$	600	3	32,4
6	1	1	$1{,}7\cdot10^{-2}$	900	3	14,4
7	1	1	$1{,}7\cdot10^{-2}$	600	4	41,9
8	1	1	$1{,}7\cdot10^{-2}$	600	5	58,7
9	1	1	$1{,}7\cdot10^{-2}$	600	6	74,4
10	1	1	$1{,}7\cdot10^{-2}$	600	7	67,8
11	1	1	$1{,}7\cdot10^{-2}$	600	8	55,7
12	1	0,8	$1{,}7\cdot10^{-2}$	600	6	54,5
13	1	0,9	$1{,}7\cdot10^{-2}$	600	6	58,8
14	1	1,1	$1{,}7\cdot10^{-2}$	600	6	70,6
15	1	1	$8{,}5\cdot10^{-3}$	600	6	24,7
16	1	1	$2{,}5\cdot10^{-2}$	600	6	36,1

The optimum capacity of the microwave radiation is 600 W (Table 1, item 5). With increasing the irradiation power the yield gradually increases. With further increase in the power of microwave irradiation to 900 W yield decreases, resinification reaction mass is observed (Figure 3).

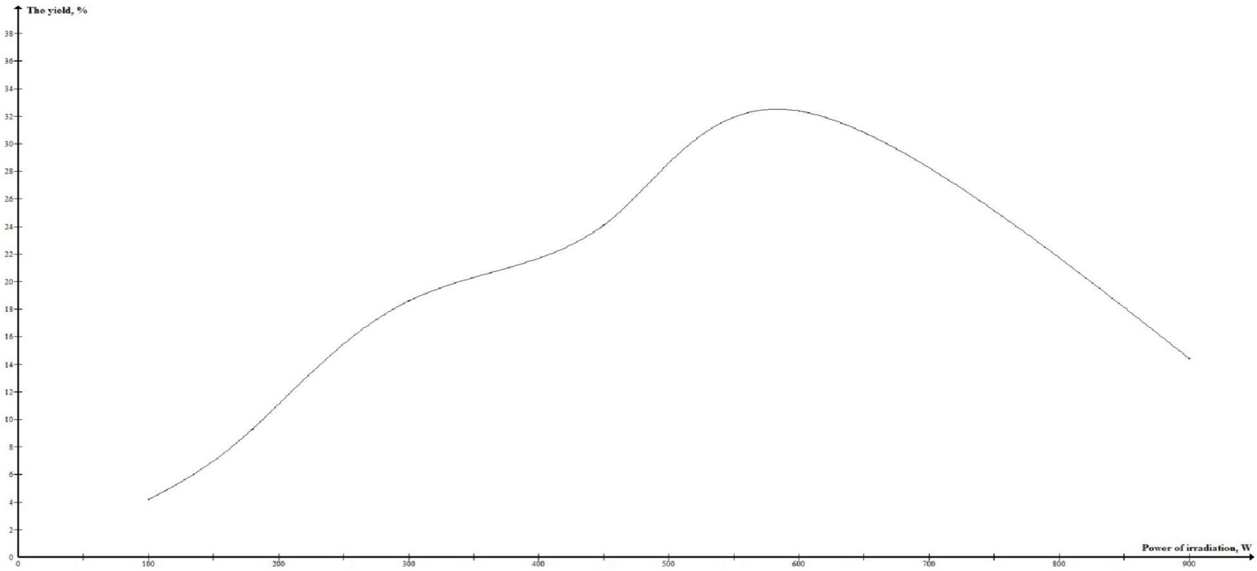

Figure 3 – Effect of irradiation on the microwave power
on output hexylbutanoate ([butanoic acid]: [1-hexene] [sulfuric acid] = $1:1:1,7 \cdot 10^{-2}$, τ = 3 min)

Further experiments were carried out with a power of 600 W. The optimal duration of reaction is 6 min (Table 1, item 9).

Effect of duration on the course of theprocess has an extreme nature, with increasing duration from 3 to 9 minutes, the yield gradually increased with a peak at 6 min, further increasing of duration leads to resinification of reaction mass and adecrease in yield of the target product (Figure 4).

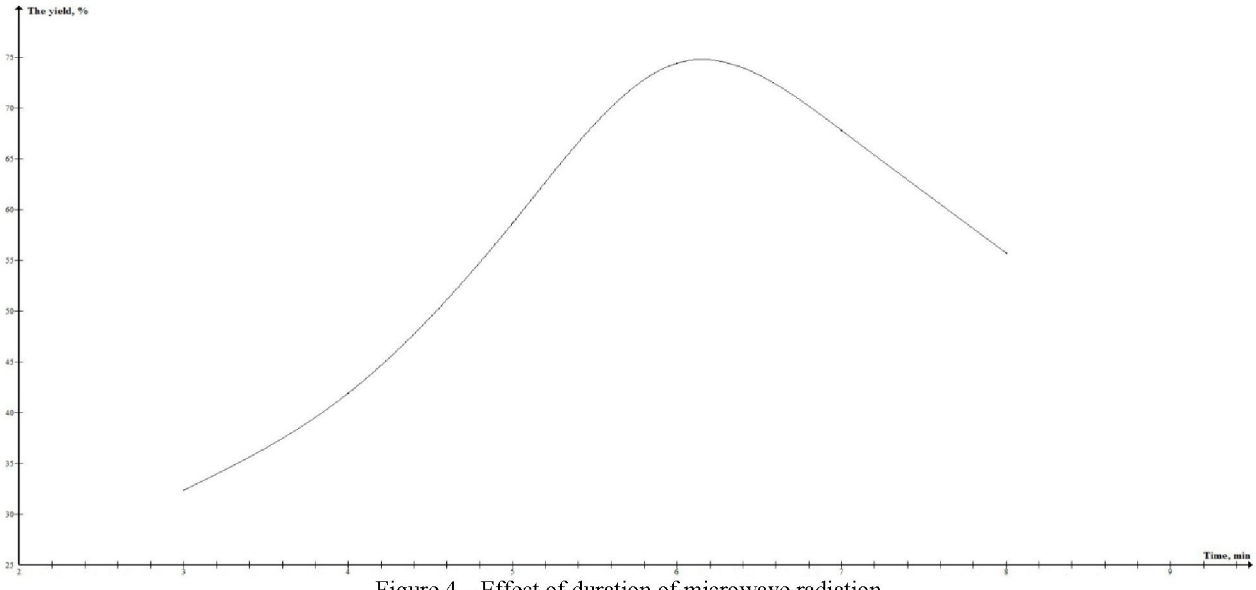

Figure 4 – Effect of duration of microwave radiation
on the output hexylbutanoate ([butanoic acid]: [1-hexene] [sulfuric acid] = $1:1:1,7 \cdot 10^{-2}$, the irradiation power = 600 W)

We also investigated the effect of the initial reagents ratio, while varying the ratio of butanoic acid and 1-hexene from 1:0,8 to 1:1,1, respectively, hexylbutanoate output gradually increases with a maximum yield at 1:1, ratio, further increase the ratio to 1-hexene butanoic acid reduces yield of product (Figure 5).

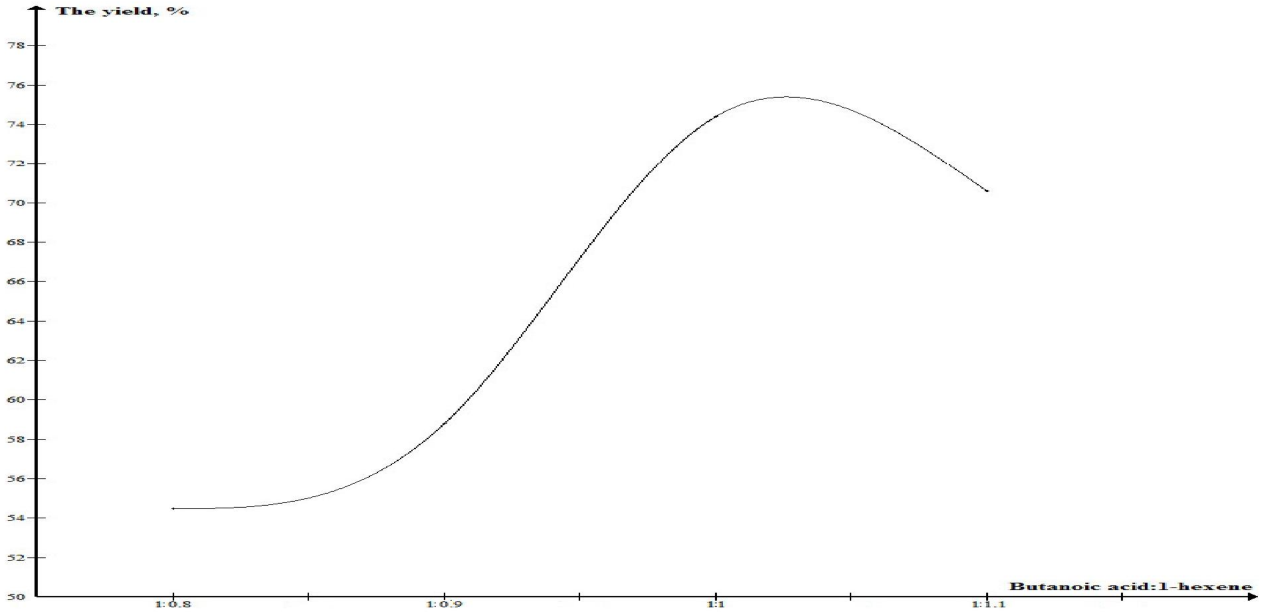

Figure 5 – Effect of the ratio of the initial reagents on the yield hexylbutanoate
(sulfuric acid = = $1{,}7 \cdot 10^{-2}$, τ = 6 min, irradiation power = 600W)

To determine the effect of the catalyst on the yield contact product runs were conducted at different molar ratios of sulfuric acid, lowering the molar ratio of sulfuric acid twice reduces theyield of product threefold, increasing catalyst ratio leads to resinification reaction mass and correspondingly reduces the yield of the product (Figure 6).

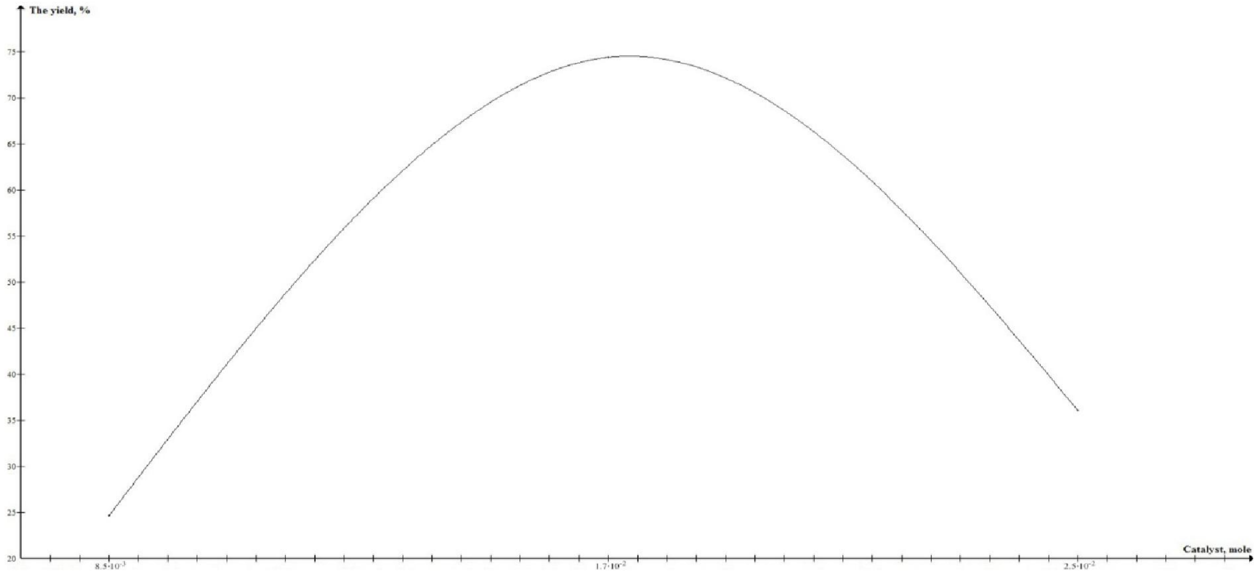

Figure 6 – Effect of molar ratio of the catalyst to yield
hexylbutanoate ([butanoic acid]: [1-hexene] = 1: 1, τ = 6 min, irradiation power = 600 W)

The optimal value of the molar ratio of the starting reactants and the catalyst is [butanoic acid]: [1-hexene]:[conc. H_2SO_4] = $1:1:1{,}7 \cdot 10^{-2}$ (MW radiation power = 600W, τ= 6 min).

As it can be seen from obtained data to determine the optimal process conditions, the most powerful influence on the course of the reaction has a power of microwave irradiation (Table 1, items 1-6, Figure 3), weakest influence has the ratio of the initial reagents (Table 1, items 12-14, Figure 5).

4 Conclusions

The possibility of using microwave irradiation in the synthesis hexylbutanoate addition reaction of 1-hexene and butyric acid in the presence of sulfuric acid. The optimum parameters of the process were determined. The optimal parameters are theratio of the starting reactants and catalyst [butanoic acid]:[1-hexene]:[conc. H_2SO_4] = 1:1:1,7·10^{-2}, the microwave irradiation power = 600 W, duration 6 minutes. With found conditions, the yield reached 74.4%. Our proposed method of obtaining hexylbutanoate, compared with the known methods can significantly reduce the duration of the process.

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ГЕКСЕН-1 МЕН БУТАН ҚЫШҚЫЛЫНЫҢ ҚОСЫЛУ РЕАКЦИЯСЫН МИКРОТОЛҚЫНДЫҚ БЕЛСЕНДІРУ

Аннотация. Микротолқындық сәулелендіру жағдайында күкірт қышқылы қатысында гексен-1-ді бутан қышқылына қосылу реакциясы арқылы гексилбутаноат (тағам және парфюмерлі өнеркәсіпте пайдаланылатын ароматизатор) синтезін жүргізу мүмкіндігі келтірілген. Үрдісті жүргізудің оңтайлы жағдайлары анықталған (микротолқындық сәулелендіру қуаты, ұзақтығы, бастапқы реагенттер мен катализатор қатынасы). Микротолқындық сәулелендіру қуатын көбейткен сайын өнім шығымы жоғарылай түседі, сәулелендіру қуатынодан әрі көбейткенде реакциялық массаның шайырлануы жүріп, өнім шығымы төмендейді. Синтезді жүргізудің ең оңтайлы жағдайы бастапқы реагенттер мен катализатор қатынасы [бутан қышқылы]: [гексен-1]: [конц. H_2SO_4] = 1:1:1,7*10^{-2}, микротолқындық сәулелендіру қуаты = 600 Вт және үрдіс ұзақтығы 6 мин болып табылады. Табылған жағдайдағы өнімнің шығымы 74,4%-ды құрайды. Реакцияның жүруіне микротолқындық сәулелендіру қуаты ең үлкен, ал бастапқы реагенттердің қатынасы ең төмен әсер етеді. Өнімнің шығымы ұзындығы 30 м және ішкі диаметрі 0,25 мм, полиэтиленгликольмен модификацияланған нитротерефталь қышқылынан тұратын HP-FFAPкапиллярлы колонкасын пайдалану арқылы газды хромато-масс спектрометрия әдісімен анықталды. Біздің ұсынып отырған гексилбутаноатты алу әдісі белгілі әдістермен салыстырғанда үрдіс ұзақтығын айтарлықтай қысқартуға мүмкіндік береді және жасыл химия принциптеріне сәйкес келеді.

Кілт сөздер: микротолқындық синтез, гексилбутаноат, бутан қышқылы, гексен-1, күкірт қышқылы, күрделі эфирлер, сәулелендіру қуаты, хромато-масс спектрометрия

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МИКРОВОЛНОВАЯ АКТИВАЦИЯ РЕАКЦИИ ПРИСОЕДИНЕНИЯ ГЕКСЕН-1 И БУТАНОВОЙ КИСЛОТЫ

Аннотация. Показана возможность проведения синтеза гексилбутаноата (ароматизатор в пищевой и парфюмерной промышленности) реакцией присоединения гексена-1 к бутановой кислоте в присутствии серной кислоты в условиях микроволнового облучения. Определены оптимальные условия проведения процесса (мощность микроволнового облучения, продолжительность, соотношение исходных реагентов и катализатора). При увеличении мощности облучения постепенно увеличивается выход целевого продукта, при дальнейшем повышении мощности микроволнового облучения наблюдается осмоление реакционной массы и снижение выхода продукта. Наиболее оптимальным условием проведения синтеза является соотношение исходных реагентов и катализатора [бутановая кислота]: [гексен-1]: [конц. H_2SO_4] = $1:1:1,7*10^{-2}$, мощность микроволнового облучения = 600 Вт, продолжительность процесса 6 мин. Выход целевого продукта при найденных условиях составляет 74,4%. Наиболее сильное влияние на ход протекания реакции оказывает мощность микроволнового облучения, наиболее слабое влияние оказывает соотношение исходных реагентов. Выход продукта определяли методом газовой хромато-масс спектрометрии с использованием капиллярной колонки HP-FFAP длиной 30 м и внутренним диаметром 0,25 мм, состоящей из нитротерефталевой кислоты модифицированной полиэтиленгликолем. Предлагаемый нами способ получения гексилбутаноата, по сравнению с известными способами позволяет существенно сократить продолжительность процесса и соответствует принципам зеленой химии.

Ключевые слова: микроволновый синтез, гексилбутаноат, бутановая кислота, гексен-1, серная кислота, сложные эфиры, мощность облучения, хромато-масс спектрометрия

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