

UDC 542.943

**ENVIRONMENTALLY SAFE CONDITIONS FOR SYNTHESIS
OF ISOBUTYRIC ACID**

**ЭКОЛОГИЧЕСКИ БЕЗОПАСНЫЕ УСЛОВИЯ
ПОЛУЧЕНИЯ ИЗОМАСЛЯНОЙ КИСЛОТЫ**

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Abstract. Isobutyric acid is used as the extractant of alkaline elements, in production of the preserving and desiccants. Perspective direction is the use of IBA is production of higher isomeric monocarboxylic acids based on it. Isobutyric acid is used limitedly of in organic synthesis due to its high cost. Isobutyric acid, as well as all lower monocarboxylic acids, mainly obtained by oxidizing the corresponding

aldehyde. However, the known methods are characterized by low output of the target acid and not high change ratio of the aldehyde. To achieve high output of isobutyric acid without the accumulation of peracids the influence of the flow rate of the oxidizing gas, temperature, duration of oxidation on peracid content, output of isobutyric acid and change ratio of isobutyraldehyde are investigated in the present work. Researches have shown that in the presence of oxygen isobutyraldehyde reacts much faster - change ratio in one hour was 86 %, whereas in the oxidation by air - 60 %. However, the rate of peracid formation in oxygen oxidation is much higher and is equal to 4,3 % of post- mix weight. An environmentally safe conditions of liquid-phase oxidation of isobutyraldehyde to isobutyric acid are also investigated. Catalyst mixture, preventing the accumulation of hazardous peracids in the reaction mixture is developed. Best results are obtained by using selected catalytic system consisting of cobalt acetate, manganese acetate and cobalt bromide, in the ratio 1:0,5:0,1. In this case, the change ratio of IBA in one hour is 94 % and the content of peracid in the reaction mixture does not exceed 1,2 wt. %. A method of recovery of isobutyraldehyde from waste gases by chemisorption of polypropylene polyamine is proposed. The obtained Schiff base are proposed as an additive to corrosion inhibitors active base.

Аннотация. Изомасляная кислота (ИМК) используется в качестве экстрагента щелочноземельных элементов, при производстве консервирующих средств и сиккативов. Перспективным направлением использования ИМК является производство на её основе высших изомерных монокарбоновых кислот. Ограниченное применение изомасляной кислоты в органическом синтезе в настоящее время связано с её высокой стоимостью. Изомасляную

кислоту, как и все низшие монокарбоновые кислоты, в основном получают окислением соответствующего альдегида. Однако известные методы характеризуются низким выходом целевой кислоты и не высокой конверсией альдегида. Для достижения высоких выходов ИМК без накопления надкислот, в настоящей работе исследованы влияния интенсивности потока окисляющего газа, температуры, продолжительности окисления на содержание надкислот, выход ИМК и на конверсию ИМА. Исследования показали, что в присутствии кислорода ИМА реагирует значительно быстрее – через час конверсия составляет 86 %, в то время как при окислении воздухом – 60 %. Но при окислении кислородом скорость образования надкислот значительно выше и составляет 4,3 % от массы послереакционной смеси. Также нами исследованы экологически безопасные условия проведения жидкофазного окисления изомасляного альдегида в изомасляную кислоту. Разработана каталитическая смесь, предотвращающая накопление взрывоопасных надкислот в реакционной смеси. Лучшие результаты получены при использовании подобранной каталитической системы, состоящей из ацетата кобальта, ацетата марганца и бромида кобальта, взятых в соотношении 1:0,5:0,1. В этом случае конверсия ИМА через один час достигает 94 %, а содержание надкислот в реакционной смеси не превышает 1,2 масс. %. Предложен способ утилизации изомасляного альдегида из отходящих газов хемосорбцией полипропиленполиаминами. Полученные основания Шиффа предложены в качестве добавки к активной основе ингибиторов коррозии.

Key words: isobutyraldehyde, isobutyric acid, peracid, liquid phase oxidation, off-gases, polypropylene polyamine, Schiff bases, corrosion inhibitor.

Ключевые слова: изомасляный альдегид, изомасляная кислота, надкислота, жидкофазное окисление, абгазы, полипропиленполиамины, основания Шиффа, ингибитор коррозии.

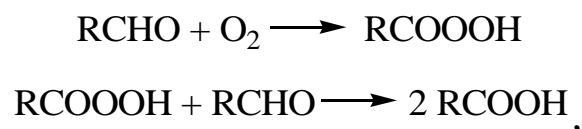
In the development of the petrochemical industry is one of the important places takes isobutyric acid, which is widely used in petrochemical synthesis for producing higher isomeric monocarboxylic acids, conservatives, plant-protecting chemicals, etc.

Nowadays, due to the development of process of cheap isobutyraldehyde obtaining from olefins and synthesis gas, preferred among other ways to obtain the isobutyric acid is the oxidation of the isobutyraldehyde [1]. Despite the presence of a sufficiently broad resource base, isobutyric acid in commercial size in Russia is not produced. This is due to lack of modern "green" ways to get [2].

Stringent environmental and economic requirements dictate the need for the creation of the isobutyric acid production technology, providing high intensification of the process and its safety. In this regard, the greatest interest is the oxygen catalytic liquid phase oxidation isobutyraldehyde.

The main environmental problems in getting isobutyric acid by liquid phase oxidation of isobutyraldehyde is the accumulation of hazardous peracids in the reaction zone and significant toxic gas emissions.

The general scheme of the isobutyraldehyde oxidation reaction has the following form:



where $\text{R} - (\text{CH}_3)_2 - \text{CH} -$.

Chromatographic analysis of the products of oxidation of isobutyraldehyde detects the presence of low molecular weight organic acids (acetic acid, propionic acid), as well as acetone isopropyl alcohol and [3].

One of the main conditions to achieve high yields of isobutyric acid without the accumulation of peracids is to ensure effective supply of the oxidizing gas to the reaction zone. The main type of processing equipment used in the chemical, petrochemical and refining industries, are machines fit with contact mass-transfer devices of various types. The research of processes and devices on the scale and conditions of industrial productions to solve the above problems is a complex and lengthy. Therefore, the synthesis was carried out in reactors of various types in vitro.

It is known that the use of the column reactor in comparison with the oxidation reactor with mechanical stirring, provides a large surface contact between the phases. Uniform distribution of liquid and gas into the column reactor facilitates the use of different nozzles. Results of our investigation of liquid phase oxidation of isobutyraldehyde showed that periodic wire Panchenkov's packing made of stainless steel mesh, perforated metal sheet, multilayer nets, etc., are more efficient than conventional contact devices. Furthermore, their extremely important advantage is a low flow resistance - in the range of 1-2 mm. Hg. (130-260 Pa) per theoretical plate.

The influence of the flow rate of the oxidizing gas, temperature, oxidation time on the content of peracids, output of isobutyric acid and change ratio of isobutyraldehyde was investigated. We have performed two

series of experiments with the use of air and oxygen as the oxidant. [2] Researches have shown that in the oxygen presence isobutyraldehyde reacts much faster – in one hour the change ratio was 86 %, while the change ratio in the oxidation with air - 60 %. However, the rate of peracid formation in oxygen oxidation is much higher and is equal to 4,3 % of post-mix weight

Formation and accumulation of peracids in the oxidation of the aldehyde to the acid can lead to explosions. To reduce the concentration of peracid in the reaction mixture, according to the literature data catalysts are widely used, mainly metal compounds of variable valence. However, most of the known catalysts have low activity, high cost and are highly toxic [4,5].

We investigated acetates of divalent cobalt, copper, manganese, iron, as well as cobalt bromide as catalysts. Catalysts were introduced, after dissolving them in isobutyric acid in an amount of 0.05 g/100g isobutyraldehyde (Table 1).

From the obtained research data of using of acetates of divalent cobalt, copper, manganese, iron, and cobalt bromide as catalysts follows that each of the examined catalysts have advantages and disadvantages [2]. Cobalt acetate and bromide are quite active as catalysts for the oxidation - they provide a high yield of the isobutyric acid, but the content of peracids thus is also high. In contrast, manganese acetate leads to a reduction of the content of peracids, but does not provide a high yield of isobutyric acid, probably due to the formation of by-products of the process. When using copper acetate as an oxidation catalyst, the lowest isobutyric acid outputs and high content of peracids was marked, in comparison with other catalysts. Consequently, it is possible to combine the advantages of these catalysts and reduce their drawbacks using catalyst systems.

Therefore, we investigated the liquid phase oxidation of isobutyraldehyde in the presence of catalyst system - the acetates of cobalt and manganese, and cobalt bromide. Results of investigations of the influence of catalytic system components on change ratio of isobutyraldehyde on and output of the isobutyric acid are given in Table 2.

Best results are obtained when using a catalyst system consisting of cobalt acetate , manganese acetate and cobalt bromide, in the ratio 1:0,5:0,1. In this case, the change ratio in one hour was 94 % and the content of peracid in the reaction mixture does not exceed 1,2 wt. %.

Table 1. Liquid-phase oxidation of isobutyraldehyde in the presence of catalysts

Name of indicators	Катализатор												
	Cobalt acetates			Manganese acetate			Copper acetate			Cobalt bromide			Mixture of cobalt acetates, manganese acetate, cobalt bromide
Time, hour	1	2	5	1	2	5	1	2	5	1	2	5	1
Change ratio of isobutyraldehyde, %	93	98	99	94	99	99	72	97	98	93	99	99	94
Output of isobutyric acid, %	80	88	90	83	89	89	69	80	89	82	88	92	84
Peracid content, wt. %	1,6	1,5	1,3	1,3	1,3	1,1	2,2	2,1	2,1	2,0	1,7	1,2	1,2

Table 2. Liquid-phase oxidation of isobutyraldehyde in the presence of selected catalyst system

Name of indicators	Mixture of cobalt acetates, manganese acetate, cobalt bromide, wt. %																				
	1:1:1			1:1:0,5			1:0,5:0,1			0,5:1:1			0,5:0,5:1			0,5:1:0,5			1:0,5:0,5		
Ratio	1	2	5	1	2	5	1	2	5	1	2	5	1	2	5	1	2	5	1	2	5
Change ratio of isobutyraldehyde, %	94	99	99	93	99	99	96	99	99	94	99	99	94	99	99	93	98	99	94	99	99
Output of isobutyric acid A, %	84	88	93	83	88	92	83	89	94	82	88	92	83	88	92	82	89	92	83	89	93
Peracid content, wt. %	1,2	1,2	0,7	1,8	1,4	0,7	1,3	1,1	0,5	1,9	1,6	1,2	1,6	1,4	0,9	1,5	1,3	0,6	1,2	1,1	0,7

Process of obtaining of isobutyric acid followed by separation of toxic gases containing a significant amount of isobutyraldehyde. It is known that for the purification of gas emissions from aldehydes methods of absorption, adsorption and thermal incineration at a temperature of 700-1200 °C are used. The described methods have major drawbacks: the complexity, multi-step process and the high cost of cleaning. The most effective and acceptable method from the point of view of cleaning gases, and from an economic point of view is the absorption method of purifying exhaust gases from aldehyde with the help of amine compounds which exhibit a high absorptive capacity relative to the aldehyde [6-8].

We investigated the process of deep cleaning of exhaust gases in isobutyric acid production from isobutyraldehyde by the mean of polypropylene polyamine, which are a mixture dipropylenetriamine, tripropylenetetramine etc.

A constant amount of isobutyraldehyde and absorber was used for synthesis. The composition of exhaust gases before and after purification was determined by chromatography. Purification of the gas mixture was conducted at a flow rate of oxidizing gas 10, 15 and 20 l / h (Table 3).

Table 3. Cleaning of the gas mixture of isobutyraldehyde in the absorber at 20 °C

Isobutyraldehyde content in gas mixture, mg/m ³		Gas mixture supply rate, l / h
Before cleaning	After cleaning	
17500	no	10
20750	trace amount	
19000	no	
15800	no	15
35120	3,51	
33750	3,22	
38550	4,11	20
35000	3,39	
51250	22,15	

As follows from the presented data, the use of absorbent polypropylene polyamine provides efficient cleaning of exhaust gases from the isobutyraldehyde. The degree of purification of the aldehyde at a flow rate of gas-vapor mixture of 10 - 15L / h reaches 99-100 %. With further increase in feed rate gas mixture to provide deep cleaning of exhaust gases from harmful impurities, it is necessary to increase the contact time of the flue gas with an absorbent material. With the decrease in the concentration of isobutyraldehyde in gas mixture and increase the contact time with the flue gas absorbent increases the degree of purification. Increasing absorbent temperature leads to a slight increase the degree of purification .

Absorbed substance dissolved in a liquid, or it reacts with it. In our case, the isobutyraldehyde removal from the gas mixture is based on the reaction of absorbent polypropylene polyamine which forms a Schiff base [2, 9, 10].

Conclusions

The obtained products have been successfully tested as a corrosion inhibitor that is used as a protective agent for oil drilling equipment and water lines from corrosion due to the action of reservoir and drainage water in reservoir pressure maintenance system and oil gathering. It was established that the corrosion inhibitor is effective to protect against corrosion in high-mineralized conditions containing hydrogen sulfide, carbon dioxide, and the dissolved oxygen.

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