

SUPERCRITICAL FLUIDS AS A MEDIUM FOR CHEMICAL REACTIONS.

F.M.Gumerov *, A.N.Sabirzyanov *, G.I.Gumerova **, F.R.Gabitov *, V.G.Nikitin *, R.A.Gazizov*.

*Kazan State Technological University, K.Marks street 68, Kazan, Russia, 420015

e-mail: gum@kstu.ru

** Academy of management TISBI, Mushtari street 13, Kazan, Russia, 420012

e-mail: ggumerova@tisbi.ru

Enhanced attention to supercritical fluids (SCF), as a medium for chemical reactions is marked in the field of supercritical fluid technologies during last decades. At present, promising opportunities and prospects of using SCF in homogeneous and heterogeneous catalysis has been already revealed in the processes of polymerization, oxidation, synthesis of materials and others.

The prosperity of using supercritical fluids as a medium for chemical reactions is conditioned by the fact, that due to high compressibility the supercritical fluid has a large free volume, which can be filled by gas molecules. For example, it is possible to achieve the concentration of hydrogen and nitrogen 10-20 times more in comparison with concentrations in traditional solvents, which are used as a medium for chemical reactions [1]. Practically complete mixing up of gases in the conditions of high concentration leads to the abrupt increase of the chemical reaction rate. The low viscosity and high diffusivity of supercritical medium lead to the reducing of necessary contact time for reagents. All these give a possibility to change stationary static reactors on running continuous-operated reactors, which have more smaller sizes, more higher indices on output, power-saving, automation and safety. It can be asserted that synthesis processes in supercritical mediums have principle technological advantages.

In one of the previous work [2] for the running unit (Fig.1) it was experimentally established that the distribution coefficient of styrene in the system water-styrene-supercritical CO₂ was equal zero within experimental accuracy in the temperature range $T=313\div 323$ ° and pressures $p=9,5\div 20$ MPa.

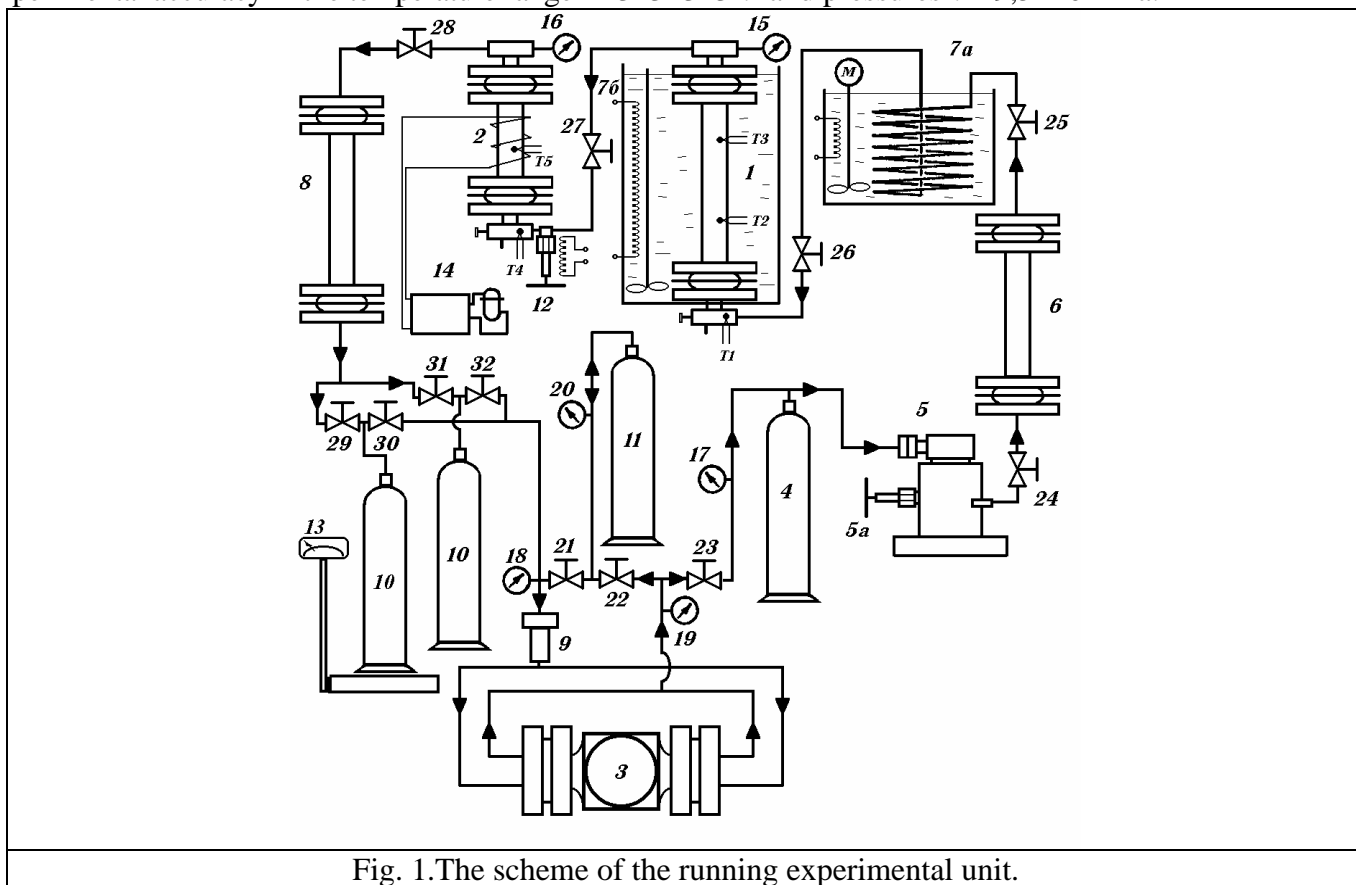
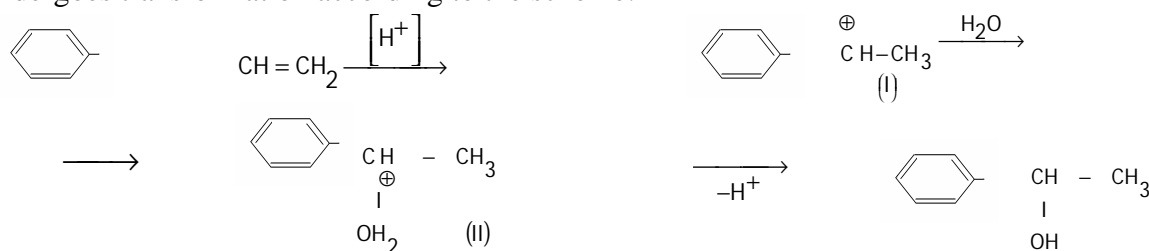


Fig. 1. The scheme of the running experimental unit.

The phase composition test has showed that initial styrene completely turns in α -phenol-ethyl alcohol. It can be concluded that synergism which takes place in multi-component systems liquid-supercritical fluid can have physical [2] or chemical nature.

In our opinion, styrene at the presence of acid reagents, which is supercritical CO_2 , ($T_{\text{cr}} = 31,1^\circ\text{C}$; $P_{\text{cr}} = 7,38\text{ MPa}$) undergoes transformation according to the scheme:



At the first stage there is a formation carbocation (I), which further forms a complex with a molecule of water (II) and further, with eliminating of proton, α -phenol-ethyl alcohol is formed. According to the schema, acid catalysis of hydration reaction of styrene takes place. Reaction is facilitated by that it is formed steady carbocation (I), which determines a direction of reaction. As it is known from the literature, the hydration of ethylene runs in hard conditions with the using of strong acids (H_2SO_4) or above Al_2O_3 at high temperatures. The α -phenol-ethyl alcohol is an important product for the perfumery industry.

The huge increase of hydrocarbon fuel consumption on a background of high rates of it's stocks reduction and appreciable ecological consequences from it's application has caused quite proved tendency in a science and technology aimed to search and develop renewable energy sources [3,7,8].

Achieved in Brasilia results on overworking of bio-mass and prospects of producing of bio-diesel fuel in USA, which estimates as 30% and more according to the volumes of traditional diesel fuel, show possibilities of such approach, which assumes that first of all it is a renewed source of energy, secondly that the environmental consequences of it's consumption is minimized. It is enough to mention sulfur absence, and to establish a fact that it's bio-decomposition in soil take place in two months. At the same time, in spite of wide distribution of these fuel in the world, the production volumes are negligible. One of the reasons is that the cost of bio-diesel fuel are higher than the same cost of traditional diesel fuel. Therefore it take place the governmental subsidies on producing of bio-diesel fuel together with large-scale investigations on the way of making it cheaper.

In opinion of several scientific groups in Germany, Japan, Australia, the prospect of solving these problem is to use supercritical fluid conditions as a solvent-extractor [6] from one side, and secondly as a medium for chemical reaction [4,5].

In particular, in the work [6], ethers of fatty acids, obtained by traditional etherification with homogeneous (or heterogeneous) catalyst, isolated from reactionary mixture with glycerin and residual methanol by sub- or supercritical extraction. It takes place the high output and exceptional purity of product.

It was mentioned that supercritical fluid condition is used as a medium for chemical reaction. And if the methanolysis in the medium of supercritical CO_2 [4] presupposes using of the catalyst, in [5] it was realized uncatalysis methanolysis in the supercritical methanol ($T_{\text{cr}} = 513,0^\circ\text{C}$; $P_{\text{cr}} = 8,04\text{ MPa}$). The same approach was realized by Japan scientists. The one conclusion on the last two investigations is that the process in supercritical conditions is more simple, than traditional process, there is no necessity for catalyst, only the removal of methanol is needed. The product output is higher and reaction finishes faster. In the following table, it is shown the advantages of this approach, also it can be noted the environmental safety and low power expenses.

Table. 1

Comparison of traditional and supercritical [5] methanolysis methods for obtaining bio-diesel fuel.

Index	Traditional method	Synthesis in supercritical methanol
Reaction duration	1-6 hour.	Up to 240 sec.
Reaction conditions	0,1 MPa , 30-65 ⁰ ?	35 MPa, 350 ⁰ ?
Catalyst	Acid or alkali	To be absent
Transformation of fatty acids	Saponification products	methyl esters
Output	97%	98,5%
During fuel purification it is necessary to remove	Methanol, catalyst and saponification products	Methanol
Process scheme	More complex	Simple

Above mentioned methanolysis in supercritical methanol was realized in present work. For realization of such process, the autoclave was made (volume 5 ml, Fig.2). It is a thick-wall, ribbed, one side closed pipe. Open side was sealed by lens with nut.

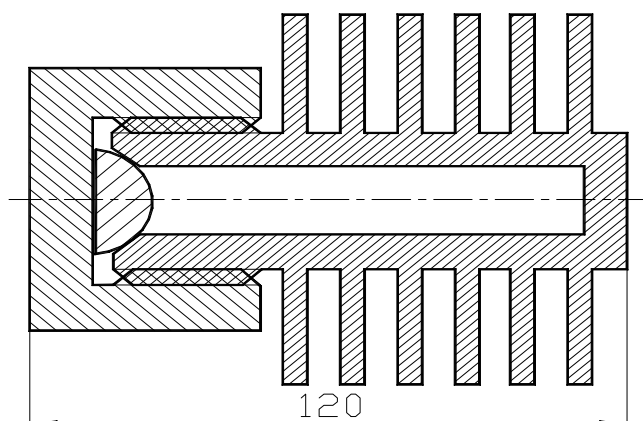


Fig.2. High pressure autoclave.

Uncatalysis methanolysis process was realized in the following way. Autoclave was fixed vertically with open side in the top. After, it was feed with rape oil and methanol (mole ratio 1:42). Autoclave was feed completely for exception air presence. For methanolysis, it is need quickly to reach supercritical parameters for methanol. It was provided by locating autoclave in tin bath (temperature $450 \div 480^{\circ}$) on $10 \div 240$ seconds. After, with the aim to abrupt reaction, autoclave was located in water bath at room temperature. After cooling, autoclave was unloaded and reactionary products were poured out in the glass volumes for precipitation and following composition test. After precipitation, the mixture divided on two liquid layers (Fig.3). The up layer contained mixture of methyl esters and methanol, the down layer contained glycerin and methanol. After, the up layer separated to another glass volume and methyl esters separated from methanol by distillation. The composition of methyl esters (Table 2) was detected by chromatograph «Chromass» (USA) with capillary column, detector is ultra-violet.



Fig. 3. Samples

Table 2

Output of methyl esters at methanolysis in supercritical conditions and classic traditional method.

? sample	Composition of initial product, gram		Process temper. ?	Pres- sure, MPa	Duration of process, sec.	Methyl esters, %						
	Rape oil	Metha nole				palmitic acid	stearic acid	oleic acid	linolenic acid	linoleic acid	arachidic acid	eruk acid
1	1.801	3.218	723	>200	240	4.62	17.91	66.70	2.02	?	2.60	6.06
2	1.616	2.926	723		100	2.38	7.64	24.85	56.15	?	1.43	7.52
3	1.597	3.181	723		20	8.44	9.67	57.32	4.21	10.66	3.47	6.20
4	1.784	3.058	723		10	12.19	3.54	51.44	7.09	19.29	1.99	4.43
5	1.838	3.339	753		10	5.86	11.45	62.56	3.35	10.61	2.23	3.91
6	1.796	3.403	753		20	3.20	5.81	25.65	16.43	37.47	?	3.40
7	1.806	3.363	753		100	9.15	2.40	55.90	4.81	19.27	2.89	5.54
Traditional method						8.98	24.17	24.81	?	8.55	14.01	19.46

Sample ? 6 of methyl esters was contained 8.01% methyl esters of myristic acid.

Authors express gratitude to the Russian fund of basic investigation for support to the present work carried out within the framework of the grant of the Russian Federal Property Fund ? 03-03-32361.

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