

Application of elementary microwave radiation for intensification of heterogeneous catalytic processes

*Maria Luzina**, *Aydar Minibaev*, and *Vladimir Ilyin*

Ufa State Petroleum Technological University, 2, Oktyabrya pr., Sterlitamak, 453118, Russia

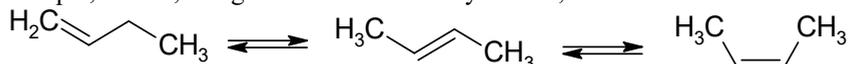
Abstract. This paper shows the results of study of effect of microwave radiation for effective energy transfer and thermal processes intensification. Big attention is paid to the processes of butene isomerization and hydrogenation of hydrocarbons. Experimental results show a significant increase in the activity of some catalysts when microwave radiation is used, which may lead to optimization of technological processes and increase their efficiency in industry. In addition to increase of catalyst activity, application of microwave radiation leads to simplification of flow sheet, since the role of the energy carrier is performed by electromagnetic radiation of the microwave range that can also increase the prospects of using microwave radiation.

1 Introduction

Laboratory studies show big opportunities for using microwaves for effective energy transfer and thermal processes intensification [1-3]. However nowadays electromagnetic radiation of super high frequency (SHF) range is limited use in world and domestic practice. In general, it is used for heat treatment and drying processes in food and forest industries.

Scientists of Sterlitamak branch of Ufa State Petroleum Technical University (USPTU), worked under a professor R.R. Daminev, made noticeable contribution to study effect of SHF radiation on chemical processes [4-6]. For example, number of publications refers to heterogeneous catalytic processes in electromagnetic field, catalytic isomerization of butenes in particular [4,6]. Studying of these reactions is of the utmost interest, since gas phase solid catalyst isomerization processes are used industrially during obtaining monomers for synthetic rubbers – butadiene and isoprene [7,8].

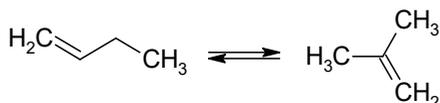
For example, butene, using in the reaction as any isomer, forms mixture of isomers.



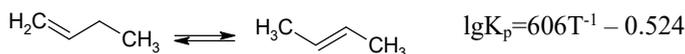
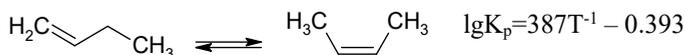
Butene equilibrium isomerization with displacement of double bond over the temperature range from 200 to 300°C follows equation $\lg K_p = 619T^{-1} - 0.335$ [6].

Partly n-butene isomerizes in isobutene

* Corresponding author: m_luzina@mail.ru



Equation $\lg K_p = 304T^{-1} - 528 \pm 0.020$ describes equilibrium of reaction of 265-426°C n-butene isomerisation.



Design values of equilibrium composition is close to obtained experimental values. In general equilibrium is possible for all of 4 butene isomers.

The most active catalyst in isomerization reaction of 1-butene into 2-butenes is Cr_2O_3 . 87-84% of 2-butenes afford from 1-butene over 250-260°C range, trans-isomer prevails. The results of experiment of isomerization of 2-butene for 25-minutes cycle SHF radiation over catalyst K-16 confirm literary data (Figure 1).

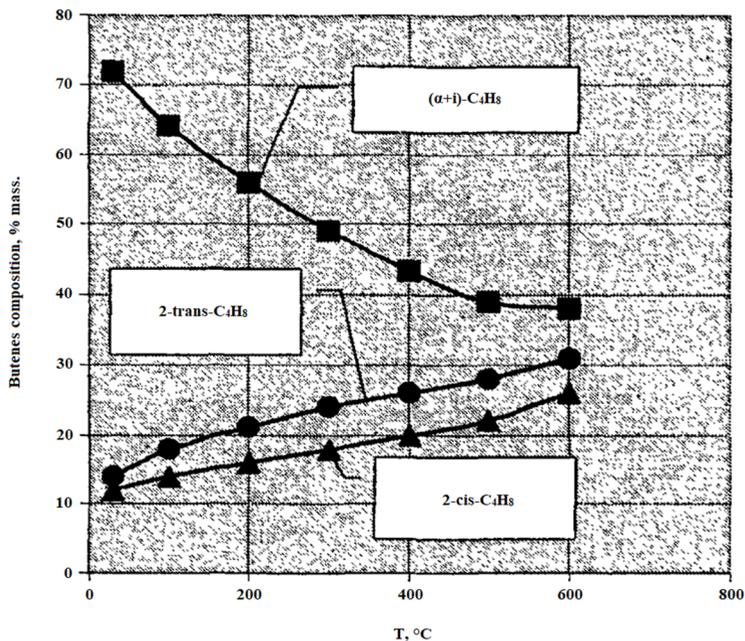


Fig. 1. Butenes composition-temperature dependence on exposure to SHF radiation, catalyst K-16U. Raw materials composition: α-butenes (1) – 79.29%; trans-butene (2) – 9.98%; cis-butene (3) – 10.73%.

2 Materials and methods

Range papers of Daminev RR with colleagues refers to studying SHF radiation effect on processes of basic petrochemical synthesis, dehydration, hydrogenation, oligomerization, which is used for synthetic rubbers production and for numbers of another processes [4-6]. In particular, SHF radiation showed high efficiency during isomeric butenes dehydration into butadien: $\text{C}_2\text{H}_8 \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}_2$

3 Results and discussion

Trial experiments shows that optimal temperature of this process is 600°C and it required to dilute with water vapour or nitrogen in volume ratio no less than 1:10. It is notable that nitrogen as diluent is more preferred than water vapour. Nitrogen molecules have more ability to penetrate in catalyst pores since their size is less than size of water molecules. Less energy is spent for diligent heating using nitrogen and thus less energy is removed from reactionary zone since nitrogen molar heat capacity is 1.7 times less than water vapour heat capacity. This is an additional factor of reducing energy consumption for synthesis. The experiment results are shown in Table 1.

Table 1. Dehydration of butenes on catalystK-16Uusing SHF radiation, T=600°C.

Dilution, mole	Volumevelocity, h ⁻¹	Contact gascomposition, % mass.								
		CO ₂	H ₂	CH ₄	C ₂ H ₄	C ₃ H ₆	Mixture of 1-butene and isobutene	C ₄ H ₈ , trans	C ₄ H ₈ , cis	C ₄ H ₆
1:5.9	200	7.08	0.78	0.5	2.72	1.04	23.11	31.00	17.53	16.24
1:5.3	600	6.73	1.01	0.3	1.88	0.93	22.67	29.44	18.86	18.18
1:5.5	800	6.52	1.12	0.27	1.34	0.67	20.21	29.34	19.82	20.71
1:10.7	200	6.81	0.97	0.4	1.51	0.75	23.19	31.63	17.42	17.32
1:9.8	600	6.34	1.18	0.3	1.23	2.01	21.36	27.14	18.47	21.97
1:10.2	800	6.28	1.20	0.25	2.06	1.15	20.79	26.96	17.93	23.38
1:19.9	200	6.74	0.90	0.31	1.99	0.59	23.65	30.33	18.47	17.02
1:20.4	600	6.12	1.19	0.29	1.72	1.13	23.49	37.23	16.59	22.24
1:20.2	800	6.15	1.29	0.30	1.81	0.40	21.16	27.70	16.54	24.65

As shown in the table butadiene butadiene yield during favourable conditions carrying process in electromagnetic field is 24.65% mass. what is commensurate with industrial process (heat carrier – water vapour), where butadiene yield is 20-25% mass. Using inert gas as diluent lead to simplification of flow sheet, since steam heating furnace is removed from processing line of butadiene production and electromagnetic radiation of SHF range performs the role of energy carrier, transforming catalyst substances into thermal energy, which is necessary for reaction.

R.R. Daminev with colleagues studied effect SHF radiation not only on destructive catalytic processes related to bond opening but on combination reactions processes, hydrogenation of unintentional hydrocarbons is rates as them [4]. With particular focus on assessment of the impact of SHF radiation on the catalyst activity. In particular, catalytic hydrogenation of piperylene, pseudocumene and triglycerides in SHF field using nickel on kieselguhr as a catalyst was studied.

The results of hydrogenation of piperylene under the action of microwaves experiments carried out in Sterlitamak branch of USPTU, showed that the activity of nickel catalyst does not exceed the activity of catalyst when the process is carried out via traditional way at the same temperature conditions.

During hydrogenation of triglycerides on nickel catalyst under the action of microwave radiation, an increase its activity is observed. At 200°C the activity of nickel catalyst on

silicon oxide using microwaves provides activity of 65%, which is 15% higher than the activity of the same catalyst when the process is carried out in the traditional way.

R.R. Daminev with colleagues used standard procedure of catalyst activity analysis for a more reliable estimate of the hydrogenation ability of nickel catalyst under the action of microwave radiation, that consists in hydrogenation of pseudocumene (1,3,4-trimethylbenzene). This object is convenient because its hydrogenation proceeds more or less without side reactions with the formation of 1,3,4-trimethylcyclohexane. The results are shown in Table 2.

Table 2. Experiment results of nickel on kieselguhr catalyst in the pseudocumene hydrogenation processes.

Activation condition	Industrial catalyst Ni/kieselguhr				
	Nickel content, % mass.	Mechanical strength, kg/tablet		Bulk density, kg/m ³	Yield 1,3,4-trimethylcyclohexane, % mass.
		P _{avg.}	P _{min}		
Initial inactivated catalyst	40.85	23	16	1300	-
Traditional hydrogenation method T=360°C under H ₂ for τ=6 hours	47.90	8.0	4.7	1150	41.30
Hydrogenation in SHF field T=360°C under H ₂ for τ=6 hours	47.67	6.3	3.58	1190	44.00
Traditional hydrogenation method T=400°C under H ₂ for τ=6 hours	52.00	8.0	4.8	1150	57.30
Hydrogenation in SHF field T=400°C under H ₂ for τ=6 hours	51.80	8.0	4.6	1170	65.00

As shown in the Table 2 1,3,4-trimethylcyclohexane yield at hydrogenation of pseudocumene in SHF field ($\nu=2450$ MHz) is higher than at the traditional method, on average by 8%.

Thus, the results of experimental studies of hydrochlorination processes on nickel catalyst in the electromagnetic field showed that the effect of SHF radiation in some cases contributes to the increase activity of the catalyst

4 Conclusion

In general, the works of R.R. Daminev and his colleagues, carried out in Sterlitamak branch of USPTU in the field of using SHF radiation allowed to increase the efficiency of number of industrial heterogeneous catalytic processes, dehydration and isomerisation of butenes, hydrogenation of piperylene and pseudocumene in particular.

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