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Application of Microwave Radiation in Petrochemical Processes

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Abstract—The influence of a 2450-MHz microwave radiation on the synthesis of cyclic acetals and heterocyclic compounds and the product yields is shown. Results of research on the development of new technologies and reactors with microwave heating for petrochemical industry are summarized.

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INTRODUCTION

The microwave range of the electromagnetic spectrum (wavelength range from 1 cm to 1 m and frequency range 30 GHz to 300 MHz) is between the infrared and radiofrequency ranges. This range has first been used in late 1930s in radars for enemy aircrafts and ships [1, 2]. Of interest is the fact that microwaves "came" from the military to public and personal consumption sphere, bypassing science and civil industry. In 1945 the American engineer P. Spenser, when working at a laboratory radar device, accidentally discovered thermal action of microwaves, designed the first microwave oven, and obtained the first patent for the method for cooking a food by means of microwaves [3].

By the present time abundant experience in using microwave radiation in industry, science, technics, medicine, and domestic life has been accumulated [4, 5]. There have been fairly few works on this issue in the domestic literature, especially educational and methodical. By contrast, abroad the application of microwaves has attracted much attention. In the USA and other countries, annual conferences on the application of microwave radiation (MWR) in scientific research and industrial processes are held, and a special journal "Journal of Microwave Power and Electromagnetic Energy" is issued.

We have published two monographs for use as textbooks, where we generalized and systematized advances in the application of MWR in organic chemistry and petrochemistry [6, 7].

When a substance is exposed to a 2450-MHz electromagnetic field, its polar or polarizable molecules are oriented concordantly with field pulsations. Since field vibrations and dipole rotation do not coincide in phase, the radiation energy transforms into the kinetic energy of molecules, the substance heats inside and over the whole bulk, unlike what happens during traditional surface heating by heat transfer. The ability to heat under exposure to microwaves is measured, first of all, by the dielectric constant ε' (Tables 1 and 2) [8, 9].

An outburst of interest in the application of microwaves in organic chemistry has been generated in 1986 by the publications of Gedye et al. [10] and Giguere et al. [11], whose employed household microwave ovens for heating reaction mixtures, and, in spite of the technical difficulties, could much shorten the time of Diels–Alder, Claisen, esterification, oxidation, and other reactions without sacrifice for their target product yields [10, 11]. Table 3 compares the results of these reactions under microwave and traditional heating.

The Ufa State Oil Technical University (USOTU) has an abundant experience in industrial application of MWR. In late 1950s through early 1960s, the USOTU performed active research into the development of microwave devices for soil hardening and reinforcement in critical sites of oil and gas pipe laying and for reinforcement of house footings. Microwave treatment imparted endowed to ground with the strength of brick or synthetic stone [12, 13].

Table 1. Dielectric constants of solvents at 25°C

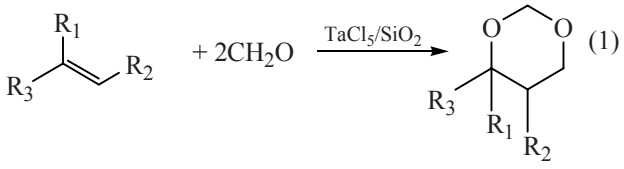
Solvent	ε'
N-methylformamide	182.4
Sulfuric acid	100.0
Water	78.5
Acetonitrile	37.5
N,N-Dimethylformamide	36.7
Methanol	32.6
Diethylene glycol	31.7
Ethanol	24.6
Acetone	20.7
Propan-1-ol	20.1
Butan-2-ol	18.5
Butan-1-ol	17.8
Pentan-2-ol	15.4
Pentan-1-ol	13.9
Hexan-1-ol	13.3
Acetic acid	6.2
Ethyl acetate	6.0
n-Propyl acetate	5.6
Chloroform	4.8
Propanoic acid	3.3
p-Xylene	2.3
1,4-Dioxane	2.2
n-Hexane	1.9

Table 2. Characteristics of dielectrics

Dielectric	ε'
Vinyplast	4.0
Genitax	7.5
Capron	4.5
Fused quartz	3.8
Nylon	4.6
E1-340-02, E2-330-02, E8-361-63, E9-342-73, E10-342-63, E11-342-63, E15-121-02 plastics	7.5–9.5
E3-340-65, E4-100-30, E5-101-30, E6-014-30 plastics	6–8
Plexiglass	2.61
Polystyrene	2.55
Polyethylene	2.26
Sapphire	11.0
Mica	5.4
S5-1 glass	3.8
S63-1 glass	12.0
Textolite	3.67
Porcelain	5.7
Freon 215	2.76
Teflon	2.0
Ebonite	2.67
Electroporcelain	5.0–8.0
Epoxide compound D1	4.0

Synthesis of Acetals

There have been a number of lines of MWR research at the USOTU, one of which involved synthesis of cyclic and linear acetals and their hetero analogs. Chandrasekhar and Subba Reddy [14] found optimal conditions for the synthesis of 1,3-dioxane derivatives by condensation of olefins with formaldehyde. The reaction mixture containing a silica-supported $TaCl_5$ catalyst was exposed to MWR. The reaction was complete within 3–4 min in 85–90% yield, whereas to reach the yield of 1,3-dioxanes of about 80% under traditional heatingrequired, on average, 10–13 h.



(1)

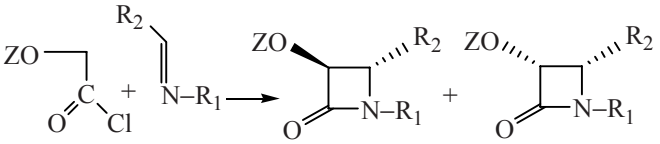
Banerjee et al. [15] reported a series of interesting reactions catalyzed by silica-supported catalysts, and the use of MWR served to drive most reactions.

Certain authors mentioned an interesting effect of MWR on the selectivity of formation of isomeric structures. Thus Bose et al. [16] found that the selec-

Table 3. Effect of microwave radiation on the rate of certain reactions

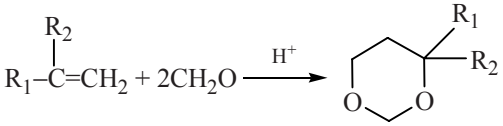
Reaction	Target product	Reaction time		Yield, %		Acceleration factor
		MWR	thermal	MWR	thermal	
Hydrolysis of benzamide	C_6H_5COOH	10 min	1 h	99	90	6
Oxidation of toluene	C_6H_5COOH	5 min	25 min	40	40	5
Esterification of benzoic acid with methanol	$C_6H_5COOCH_3$	5 min	8 h	76	74	96
Esterification of benzoic acid with propanol	$C_6H_5COOC_3H_7$	18 min	7.5 h	86	89	25
Esterification of benzoic acid with butanol	$C_6H_5COOC_4H_9$	7.5 min	1 h	79	82	8
Synthesis of phenyl benzyl ether	$C_6H_5OCH_2C_6H_5$	3 min	12 h	74	72	240

tivity of formation of *cis*- and *trans*-1,2-disubstituted β-lactams varied with varied radiation power. The *cis* form prevailed at a lower radiation power and the *trans* form at a high radiation power (Table 4).



(2)

We have studied the synthesis of 4-phenyl-1,3-dioxane and 4-methyl-4-phenyl-1,3-dioxane under MWR in a water–organic binary system. It was found that exposure to microwaves accelerated the reactions 2–6 times at the boiling point of the reaction mixtures. Probably, microwave heating favored enhanced interphase mass exchange [17].



(3)

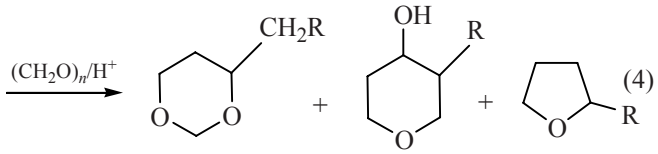
R_1 = H, CH_3; R_2 = Ph.

Table 4. Variation of β-lactam isomer ratio at varied radiation power and heating time

Heating time, min	Temperature, °C	*cis/trans* ratio, %
1	69	16/84
2	75	20/80
3	94	45/55
4	96	45/55
5	112	55/45

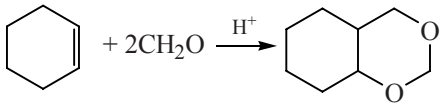
It was found that the conversion of terminal C_7–C_9 olefins and the yield of oxymethylation products (1,3-dioxanes, tetrahydropyranols, and tetrahydrofurans) under microwave heating were, too, 2–8 times higher. The composition of the reaction products was independent on the heating mode [18].

CH_2=CH–CH_2–R



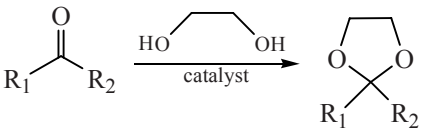
(4)

Similar results were obtained in oxymethylation of cyclic olefins [reaction (5)], in particular, cyclohexene. The conversion of cyclohexene into 4,5-tetramethylene-1,3-dioxane of about 75% was reached after 35 min of microwave heating and 85% after 4 h of thermal heating [18].



(5)

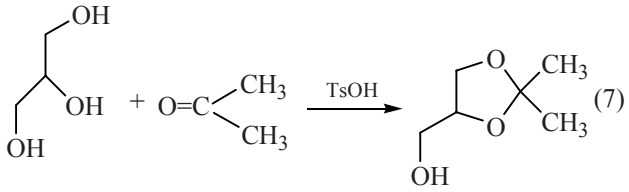
The synthesis of 1,3-dioxolane derivatives by the condensation of ethylene glycol with ketones and aldehydes under MWR and using several types of acid catalysts was studied. High yields of dioxolanes were obtained (70–90%). The reaction time under MWR was as short as 2 min [19].



(6)

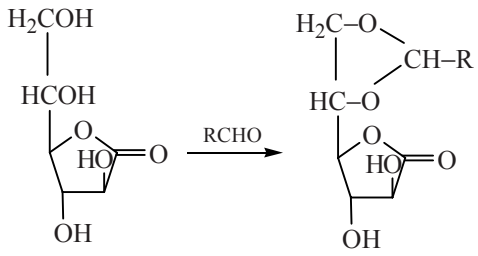
Catalysts: *p*-toluenesulfonic acid, $FeCl_3$, Al_2O_3 (Table 5).

The yield of isopropylideneglycerol (2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane) in the presence of *p*-toluenesulfonic acid (TsOH) in a flow microwave reactor at 133ºC in 1–2 min was 84%. To obtain a comparable yield on thermal heating required 12–24 h (Table 5) [20].



(7)

The acetylation of a lacton with aldehydes [reaction (8)] occurs under reflux in DMF in the presence of sulfuric acid for 24–48 h. In a microwave system and in the presence of a montmorillonite-supported KSF catalyst, the acetylation product was obtained within 10 min in a 3-fold higher yield [21].



(8)

Thus, the use of MWR makes it possible to strongly shorten the reaction time and, in certain cases, to improve the yield of target products. The great advantage of microwave heating is low contents or complete absence of polymerization or compaction products.

One more line of our research is development of technologies based on microwave heating as a single energy source [22–27].

Over the past years we have performed research aimed at intensifying industrial petrochemical synthesis reactions, such as dehydrogenation of butane and butane to butadiene, thermocatalytic cleavage of 4,4-dimethyl-1,3-dioxane into isoprene, oligomerization of hydrocarbons, etc. A feature of the cleavage of 4,4-dimethyl-1,3-dioxane into isoprene under MWR is that the reaction can be performed in the absence of catalysts, which much simplifies and accelerates the process.

A microwave technology of the production of buta-1,3-diene (major monomer in the synthesis of synthetic rubber) by dehydrogenation of *n*-butenes. The essence of the technology is that a cold raw material (1- and 2-butenes) is passed over the catalyst which serves as a receiver of MWR (2450 MHz), and 1- and 2-butenes slightly absorb radiation. Heat release occurs due to polarization of the oxide catalyst. Thus, the catalyst serves as a receiver of microwaves, a source of thermal energy for dehydrogenation, and preserves functions characteristic of an usual heterogeneous catalyst. As a result of these studies we determined optimal reaction conditions for the most effective industrial catalyst K-16u, at which the butadiene yields are 20–25 wt %.

Table 5. Yields of 1,3-dioxolanes at varied substituents and catalysts

Starting aldehyde (ketone)	Yield of 1,3-dioxolanes, %		
	p-toluenesulfonic acid	$FeCl_3$	Al_2O_3
Heptanal	96	97	75
Benzaldehyde	81	77	90
m-$O_2NC_6H_4COCH_2Cl$	98	88	90
o-$MeOC_6H_4CHO$	90	95	92
$PhCH_2CH_2CHO$	88	91	95
p-Nitrobenzaldehyde	97	83	96
p-Chlorobenzaldehyde	96	97	91
Cycloheptanone	88	85	63

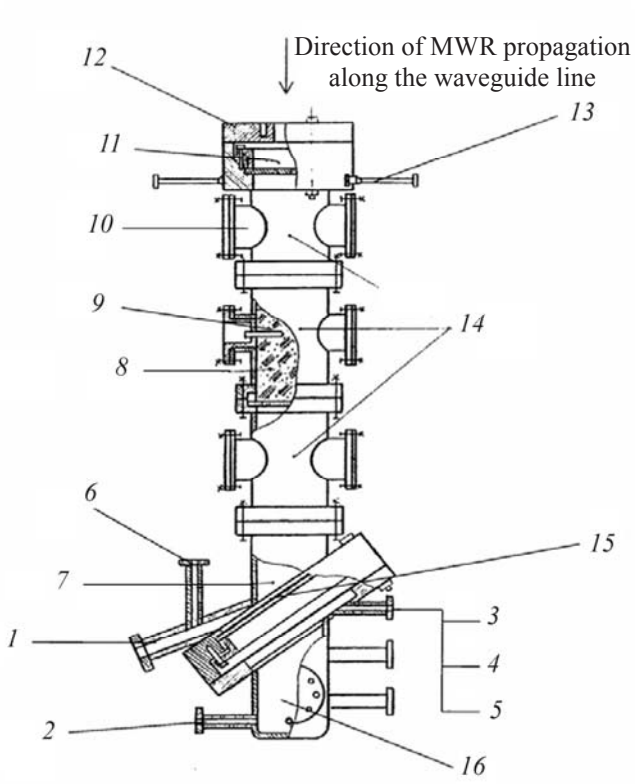
It should be specially mentioned that MWR exerts no direct effect on the catalyst structure at temperatures that cause no phase transformations.

A feature of microwave dehydrogenation, unlike thermal, consists in raw material can be fed to the reaction zone without preheating, and this offers a great advantage of reducing energy consumption for preparation of raw material, since the most part of radiation energy in heterogeneous catalytic processes under MWR transforms into heat inside the catalyst bulk.

Design of Microwave Reactor

Based on the results of laboratory studies, we developed a special reaction installation for performing endothermic processes under microwave heating. A scheme of the microwave reactor is shown in the figure. The installation comprises a continuously working MWR source with a fixed vibration frequency of 2450 MHz and a controlled output power of 0–5 kW.

The reactor (an MWR resonator) looks like a vertical cylindrical thermally isolated vessel and



(*1*) Outlet for catalyst particles, (*2—5)* water inlets and outlets, (*6)* contact gas outlet, (*7*) outlet block (top part), (*8*) catalyst, (*9*) thermocouple pocket, (*10*) hatch, (*11*) inlet block, (*12*) adapter plate, (*13*) inlet for feeding raw material, (*14*) reaction block, (*15*) Teflon cap of matching chamber, (*16*) outlet block (matching chamber).

consists of three principal blocks: inlet for raw material and MWR, reaction zone, and outlet for reaction products.

The upper cap of the reactor plays the role of radiating antenna that provides a uniform energy distribution over the reactor cross-section. The reactor should be made of 8X18H10T alloy steel resistant to aggressive media over a wide temperature range and sufficiently electroconductive. The latter is required for preventing losses of electromagnetic energy.

The inlet block is provided with a Teflon membrane for hermeticity of the reaction zone. Raw material is delivered tangentially, and the outgoing gas leaves at the bottom. The reaction chamber is equipped with distribution grids for catalyst, made of microwave-permeable heat-resistant ceramics.

In the outlet block, there is a matching chamber for residual MWR absorption. Residual radiation is incompletely absorbed by catalyst substance, penetrates through the membrane of the matching chamber, and is absorbed with water. The skew surface of the matching chamber attenuates direct reflection of MWR to magnetron. Ground catalyst particles are collected in the matching chamber.

When designing the matching chamber we introduced additional units for operation with liquid media. The chamber is equipped with a hatch, and the liquid level in the chamber can be controlled with fittings. Monitoring and measurement instruments are built in the hatch cap.

The advantages of the reactor include the possibility of operating over a wide temperature range and resistance to aggressive media. For the construction material of the reactor we chose alloy steel which gave a good account in petrochemical industry for fabricating various apparatuses and equipment.

Due to the block construction of the reaction zone, reactor dimensions can be varied, therewith preserving the height-to-diameter ratio. This ratio can be varied from minimum values to 9.75 and realized by removing from or adding to the construction one or more reaction-zone blocks.

The reactor radically differs from those presently employed in industry in the mode of energy supply to the reaction zone, which much reduces energy consumption, facilitates control of the technological process, and improves the reactor's performance. Our designed microwave reactor is almost double as efficient as reactors with thermal heating: The performance factor of the microwave reactor is 9.1% and that of an adiabatic industrial reactor is 4.6%.

It is also important that the developed reactor is an ecologically friendly device. It produces no atmospheric emissions, unlike superheaters, and consumes less water which is used exclusively in a closed cycle for cooling magnetron and circulator, as well as a matching load. The total performance factor of the microwave installation is 1.2 times as high as those of existing industrial installations.

The reactor was used for performing other endothermic processes, in particular, hydrogenation of hydrocarbons (piperylene, triglycerides, pseudocumene) on a nickel catalyst. Technologies and devices for limestone calcination, evaporation of liquid media, and drying of friable and paste-like chemical products under microwave heating were also developed.

Catalyst Regeneration in the Electromagnetic Field

In the development of petrochemical microwave processes, proper allowance must be made for auxiliary technological operations, specifically catalyst regeneration in the electromagnetic field.

The results of experimental research into regeneration of commercial oxide catalysts under the action of MWR (deposited carbon burning) allow us to give comparative characteristic of the suggested technology. For example, after traditional thermal regeneration of K-24I commercial catalyst with the carbon content of 1.9 wt %, as little as 32% of carbon is burned out. In the case of MWR after the same time, the carbon residue after regeneration is 0.9 %, i.e. 53% is burned out. The better regeneration of K-24I catalyst results in that its service period is prolonged by 40 h, which can be considered as a positive effect of MWR.

Thus, our research showed that the use of microwave radiation drives petrochemical processes, enhances their selectivity and product yield, and improves energy characteristics of industrial processes.

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