Kinetic Investigation on Direct Hydration of *n*-butene in a Multiphase Reactor

DIANA CURSARU[1]* ULRICH KUNZ[2]

[1] Universitatea Petrol – Gaze Ploieşti, 39 Bucureşti Blv., 100520, Ploieşti, Romania
[2] Technische Universität Clausthal-Zellerfeld, Germany

The microkinetics for the liquid phases synthesis of secondary butanol (SBA) from water and n-butenes using a macroporous sulfonic acid ion exchange resin as catalyst (Amberlyst DT from Rohm & Haas) was experimentally measured in a high pressure reactor (an improved version of the Carberry reactor) that enables the visualization of the phases that occur during the hydration reaction. A first set of experiments was performed in order to determine the reaction conditions where the surface reaction is the rate limiting step and where there are no influences of either external or internal mass transfer processes. Following these experiments we concluded that kinetic studies should be conducted at 800 rotation per minute stirring speed, at a temperature between 117 and 130°C on catalyst particle dimensions below 0.71 mm, at 60 bar pressure. Under these reaction conditions the surface reaction has been found to be the rate limiting step. The experimental results are well described by a four-parameter model based on Langmuir-Hinshelwood rate expression, in terms of liquid phase fugacities calculated from the predictive Soave-Redlich-Kwong (PSRK) equation of state with UNIQUAC liquid-liquid equilibrium.

Keywords: secondary butanol synthesis, microkinetic model, multiphase reactor

The hydration of 1-butene to secondary butanol catalyzed by strong acidic ion exchange resins is an alternative route to the conventional homogeneous, indirect hydration process catalyzed by sulfuric acid. Secondary butanol is a commercially interesting alcohol mainly due to its use for MEK (methyl ethyl ketone) production.

Both n-butenes hydration processes are licensed on industrial scale, for many years now, the indirect process since 1931, and the direct process since 1983. In the last years, the tendency is to replace the old, polluting process (i.e. the indirect process) with the environmentally friendly process that is the direct hydration. The indirect process is still in use due to the following advantages: low temperatures and pressures, use of hydrocarbons feeds at low olefin content, etc. Despite of these advantages, a major drawback is the use of a highly corrosive reagent that requires large energy consumption for regeneration.

The major advantage of the direct process is the elimination of the sulfuric acid and of all the consequences derived from its utilization in the process. However, the conditions used in the direct process are more severe because of a relatively lower activity of the catalyst requiring higher temperatures in order to obtain reasonable reaction rates, and higher pressures in order to compensate the effect of higher temperatures on the olefin volatility. Although the direct hydration of butene is an industrial scale process since 1983, very few kinetic data were published so far [4, 13]. We have therefore investigated the intrinsic rate of SBA formation accounting for the influence of the external and internal mass transport phenomena.

Experimental part

The laboratory plant

A schematic representation of the laboratory plant used to investigate the kinetics of the hydration of butene is presented in figure 1.

The laboratory plant consists of two important modules: the reaction system and the analytical system (fig. 3). The reactant, water, is kept in a tank (B-03) and the olefin is kept in a bottle (B-02), pressurized by nitrogen (B-01). The reactor (R-01) is two-phases operated. It is necessary to control the hold-up of both phases independently of the inlet composition. This is realized by two magnetic valves (V-03) and (V-04). Another two magnetic valves (V-01) and (V-02) are installed on the olefin and the water pipes in the suction lines of the HPLC pump (P-01). The magnetic valves can be switched independently [7].

Different volumetric water/olefin ratios can be achieved by this arrangement. The reactants are then combined and fed by means of a high pressure HPLC-pump (P-01) into the reactor (R-01). Directly in front of the pump a filter (F-01) is connected to protect it against suspended solids. Into reactor the olefin and water are converted to alcohol, whereby the alcohol is extracted by the olefin phase. The reactor has two outlet lines.

In both lines two filters (F-02) and (F-03) are inserted to protect the downstream equipment against catalyst particles. Small but representative samples are taken out off the reactor outlet line by a sample injector (ROLSI-Rapid On-Line Sample Injector). The rest of the products is sent to a phase-separation vessel (A-01) and the not consumed butene is fed to a burner. Qualitative analyses of the reaction products are finally made by a gas chromatograph HP 5890 series II model.

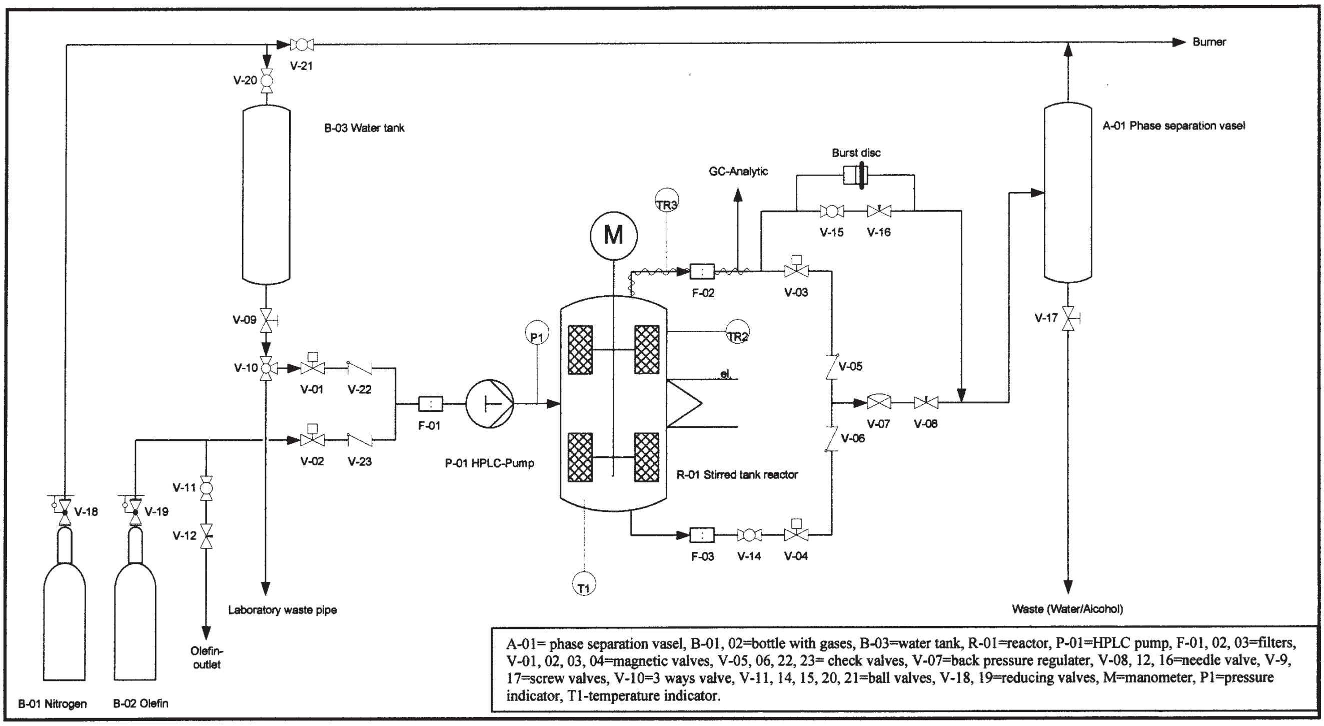
The experimental reactor

The central part of the reaction system is the chemical reactor. In this work a newly developed reactor designed for liquid-liquid reactions was tested and operated to receive kinetic data [8].

The chemical reaction of butene with water is a reaction between two reactants with a low solubility. To increase the solubility of butene in water it is obviously necessary to chose reaction conditions to keep the reactants in liquid phase. The reactants have a partial miscibility due to their low solubility. Therefore the reactor has two liquid phases: the olefin phase (as the upper one) and the water phase (as the lower one).

---

* *email: dianapetre@yahoo.com; Tel.: 0244556445*



A-01= phase separation vasel, B-01, 02=bottle with gases, B-03=water tank, R-01=reactor, P-01=HPLC pump, F-01, 02, 03=filters, V-01, 02, 03, 04=magnetic valves, V-05, 06, 22, 23= check valves, V-07=back pressure regulater, V-08, 12, 16=needle valve, V-9, 17=screw valves, V-10=3 ways valve, V-11, 14, 15, 20, 21=ball valves, V-18, 19=reducing valves, M=manometer, P1=pressure indicator, T1-temperature indicator.

Fig. 1. Schematic representation of the laboratory plant for olefin hydration [10]

Because in the industrial reactor the status of the catalyst is not well defined (it is not known to what extend the catalyst is contacted by water or olefin) and taking into account all these drawbacks of the butene hydration system, it was necessary to design a laboratory reactor that enables a visible control of the two-phases separation line, of the attachment of the catalyst in a well defined place and adjustment of hold-up independently from the feed ratio and the progress of the chemical reaction as well [8, 9, 20]. In addition, our study was focused on determining the kinetics for butene hydration reactions, but for kinetic investigations a gradientless reactor seems to be more attractive due to its features: a constant reaction rate in all the reaction volume and the absence of concentration and temperature gradients due to its hydrodynamics [1, 8].

A laboratory reactor able to fulfill all these requirements is the basket-type mixed flow reactor also known as Carberry reactor. This reactor is designed for heterogeneous catalyzed gas phase reactions or liquid reactions in one homogeneous phase.

Own reactor is a development of the Carberry reactor due to its suitability for more complicated reaction systems like heterogeneous liquid/liquid/solid reaction. Each of eight cages, containing one layer of pellets, behaves like a differential reactor which is swept through the fluid environment some thousand times per minute.

The laboratory reactor used in this work has two windows made of high pressure resistant glass, allowing the observation of the mixing behaviour inside the reactor. In addition, the windows allow the control of the hold-up and if necessary the windows can be also dismantled and replaced with a measuring sensor for FTIR spectrometer (**F**ourrier **T**ransformed **I**nfra **R**ed spectrometer) used to measure the changes of the reactants and products concentrations in time. This reactor has one feeding tube near to the separation line level and two outlet tubes, arranged at different heights. One is on top of the organic phase the other is located at the bottom of the water phase.

The stirrer of the reactor is divided in two identical sections, one rotating in the organic phase, the other in the water phase. This ensures well defined conditions for the catalyst.

The reactor can be operated up to 200 bar and temperatures up to 200°C and has a free volume of 100 mL and the reaction volume is approximately 80 mL. The material for gaskets of the windows is made of fluorinated elastomer (Kalrez) while the material for the sealing of the reactor cover is Teflon.

The operation of this reactor requires an adapted feed ratio control and simultaneously a control of the reactor outlet flow, independently from each other. This can be achieved with a pulse-width modulation of the two reactants [7]. A high pressure HPLC-pump was used to feed the reactants into the reactor. To achieve the desired feed ratio the inlet side of the pump is separated in two tubes, the first is connected to the butene bottle, the second to the water tank. To ensure the same pressure inside the two liquid reservoirs, the water tank and the butene bottle are connected to a cylinder with pressurized nitrogen. The butene bottle is under pressure keeping the butene in the liquid state, avoiding cavitation problems in the pump during suction. In figure 2 the method of the reactor feeding and the reactor outlet control are depicted.

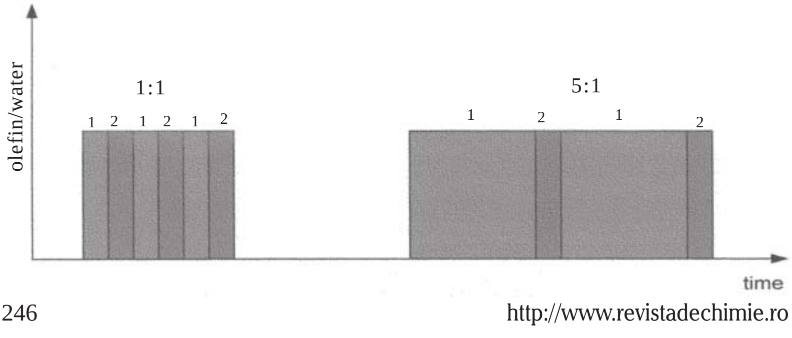


Fig. 2. Method of feed control and outlet flow control by independent pulse-width modulation of the two streams [7] (1 - color-olefin stream, 2 - color-water stream)

Table 1
THE TEMPERATURE PROGRAM OF THE GC

Split ratio	Carrier gas velocity through the column $\frac{cm}{s}$	Column head pressure kPa	Temperature program			Injector temperature °C	Detector temperature °C
			Initial temperature °C	Final temperature °C	$\frac{dT}{dt}, \frac{°C}{min}$		
20:1	20	40	40	200	20	200	220

Two magnetic valves, alternately switched allow the control of the desired feed ratio just by setting the on/off-ratio to an electronic device. A similar arrangement of two magnetic valves is used to set the reactor outlet flow ratio of the two phases. This arrangement allows feed ratio control independent by hold-up and progress of the chemical reaction during the residence time in the reactor with only one single high pressure pump.

Both outlet streams lead to the analytical equipment; the main stream passes a back pressure regulator that allows adjusting the desired operation pressure of the reactor [20].

The analytical system

For the measurement of the composition of the reaction mixture a Hewlett-Packard 5890 Series II gas chromatograph was used. This gas chromatograph is equipped with a separation column SPB-1 type of the Supelco Company, suitable to separate the olefins and the corresponding alcohols. A heat conductivity detector (TCD) able to detect not only alcohols and olefins but also water was applied. The temperature program of the gas chromatograph for the olefin hydration and more details about the separation column are presented in table 1.

To investigate the kinetics in the olefin hydration systems was mandatory to have a very good reproducibility of the outlet composition analyses with relative errors smaller than 3%.

Because the reaction mixture contains compounds with different boiling temperatures the compound with the lowest boiling point starts to boil before the others, producing bubbles on the liquid phase that is being vaporized, and as a result a random fluctuation of the pressure and a small substance separation effect occur. This effect is a consequence of low reproducibility of the analyses [14].

The solution for these drawbacks was a rapid on-line sample injector (ROLSI) (a detalied description of ROLSI is given in [10]), able to take a small sample under reaction conditions and to evaporate it in a flow carrier gas for the gas chromatograph [19]. By applying ROLSI the reproducibility was significantly improved. The average of the relative error concerning the concentration measurement of the sec-butyl-alcohol was about 1 %.

A flow sheet of the analytic system is depicted in figure 3.

The sample injector is inserted directly behind the reactor on the olefin phase outlet, due to the bigger quantity of the main product concentrated into this phase (the alcohol is extracted from the water phase by supercritical butene).

The water used in our investigation was distilled water produced in our laboratories, the butene bottle was supplied by our industrial partner SASOL Germany, the composition of this bottle is given in table 2 (we used for kinetic investigation the same butene as used in the industrial

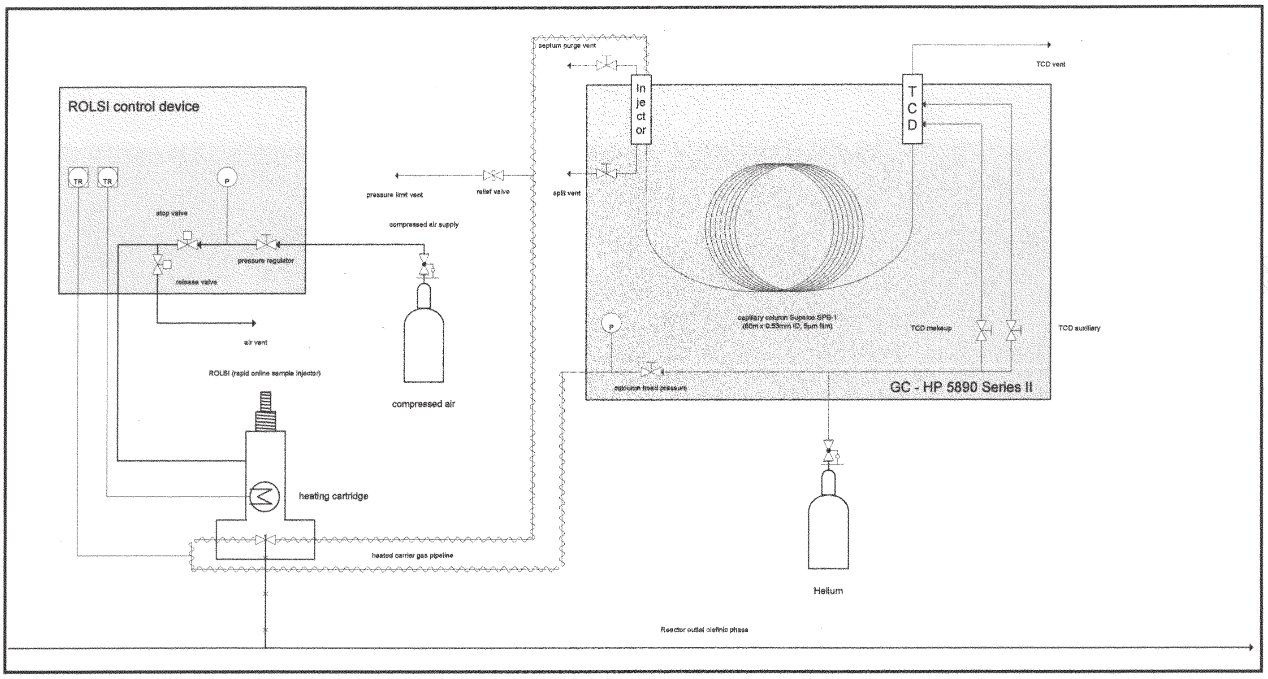


Fig. 3. Schematic of the analytic system for the olefin hydration laboratory plant [14]

plant), and the secondary butanol (99.8%) was provided by Sigma-Aldrich.

Table 2
THE MASS COMPOSITION OF THE BUTENE FEED

Compound	wt %
n-butane	0.68
iso-butane	0.08
cyclo-butane	0.02
1-butene	51.53
cis-2-butene	13.29
trans-2-butene	33.23
iso-butene	1.02
others	0.15
Total	100

The catalyst used in our investigation is a strong acid ion exchanger, its matrix is built of polystyrene divinylbenzene copolymer and the functional groups (-SO$_3$H) are introduced in a sulfonation step. The catalyst has the commercial name Amberlyst DT and was provided by SASOL Germany and it was delivered in swollen form.

A first set of experiments were performed aiming to identify a window of operating parameters where the surface reaction is the rate limiting step, that is where there are not external, nor internal diffusion limitations of the reaction kinetics.

Table 3
AMBERLYST DT-TECHNICAL DATA*

Physical form	Dark brown beads
Ionic form as shipped	Hydrogen (98 %)
Concentration of acid sites	$\geq$ 2.55 eq/kg - 0.9 eq/L
Moisture holding capacity	53 to 59 % (H^+ form)
Shipping weight	770 g/L (48.0 lbs/ft^3)
Fines content	< 0.425 mm : 0.5 % max
Surface area	36 m^2/g
Average pore diameter	220 Å
Maximum operating temperature	190°C (375 °F)

* the technical data are given by the Amberlyst DT suppliers-Rohm & Haas

External mass transfer experiments

In order to measure the rate of the external mass transport processes the stirring speed was varied. It is well known that increasing the stirring speed leads to a faster transport of the reactants to the outer surface of the catalyst and, thus to the active sites of the catalysts, and also accelerates the diffusion of the products from the active sites to the bulk fluid.

The experimental tests of secondary butanol synthesis were investigated in a gradientless reactor with a volume of 77 mL. The solid catalyst - Amberlyst DT (3 g) - was placed into the baskets attached to a rotating shaft stirred magnetically.

As demonstrated elsewhere [10] a steady-state catalytic activity of the Amberlyst DT is obtained only after 1000 h of operation. We have therefore used in our experiments a catalyst that was previously aged for 1200 h. The characteristics of the catalyst used in our investigations are presented in table 3.

The experiments performed previously with the catalyst located in the upper basket placed into the organic phase, lead to an undesirable by-product di-secondary-butyl-ether (DSBE); therefore, in order to avoid the side reaction, the catalyst was placed only in the baskets located into the water phase.

The chemical reaction between water and butene takes place on the internal surface area of the catalyst on its active sites. The chemical reaction is promoted by the transport steps: the mass transfer of the butene from the organic phase, through the boundary between the phases, to the water phase and further to the external and then to the internal surface area of the catalyst. The main product, secondary butanol, formed in the hydration reaction is desorbed and then transported into the water phase. Secondary butanol is extracted from the water phase by supercritical butene.

The experimental evaluation of the performance in butene hydration was conducted at three different temperatures (120, 140 and 155°C), at constant pressure (60 bar), using the same amount of catalyst (3 g), working at constant space time (47.9 gcat/mol/min), but 5 different stirring speeds (250, 400, 550, 700, 850 RPM). The butene:water mixtures (80:20 volumetric ratio) were fed into the reactor. Stirring started after achieving the reaction temperature and pressure. For each stirring speed 4 or 5 significant measurements were recorded with the mean relative error less than 3%. The average value of these results was considered the valid experimental point corresponding to the reaction parameters tested.

The experimental results show that the rate of the forward reaction is independent of the stirring speed above 700 RPM. These results are in agreement with those obtained on a similar catalyst [15-18].

Therefore, all further experiments were performed at 800 RPM to make sure they are conducted in a domain free of external diffusion influence.

Internal mass transport experiments

The internal diffusion influence on process kinetics depends on the catalyst particle size, the intrinsic activity of the catalyst, the reaction temperature and the catalyst texture [5, 6, 9]. Because the influence of the intrinsic activity of the catalyst and of its texture exceeds the purpose of our investigation we focused on the influence of the size distribution of the catalyst particles and the reaction temperature.

With increasing temperature, intraparticle mass transport limitations are expected to grow due to its stronger influence on the surface reaction as compared with the influence on effective diffusion coefficients inside the pores network.

It was predicted that, for a common resin (XE-307) used in the butene hydration, at a particle size of 0.8 mm (typical size of commercial ion exchangers) intraparticle diffusion limitations have to be taken into account at temperatures above 115°C [13].

In the literature only few data are available to predict the diffusional resistances in ion exchange resin particles.

The region where the internal mass transport is the rate limiting step was determined by varying the catalyst particle size. The experiments were performed under the same conditions of temperature (120, 140 and 155°C), pressure (60 bar), space time (47.9 gcat/mol/min) and volumetric butene to water ratio (80:20) as those chosen for the external diffusion tests.

For the internal diffusion tests, 4 particle sizes of the catalyst were used. The same investigations were conducted for the whole distribution of catalyst particle sizes used in industrial reactors.

The results of the internal mass transport investigations proved that the observed reaction rates depend on the particle size of the catalyst. Since the temperature was constant during the investigations, only internal mass transfer by diffusion in macroporous catalyst affects the observed rates of reaction. The goal of the following experiments was to eliminate the influence of diffusion by decreasing the size of resin particles.

Therefore, all diffusions experiments proved that for stirring speeds higher than 800 RPM we are in a domain free of external diffusion and all the kinetic experiments were performed at 800 RPM. The experimental results depicted in figure 4 proved that we are in a domain free of external diffusion and the effect of internal diffusion can be neglected for catalyst particle dimensions below 0.71 mm and temperatures lower than 155°C.

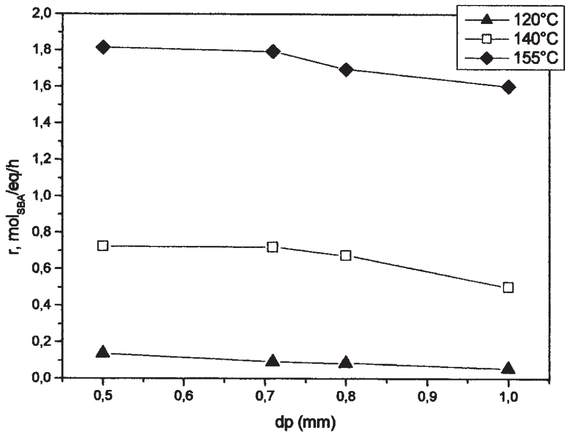


Fig. 4. Effect of the catalyst particle size on reaction rates in SBA synthesis on Amberlyst DT (T=120, 140, 155°C, p=60 bar, 80:20 vol. butene:water)

Determination of the reaction rate

The reaction between butene and water is slow and the conversion level in industrial reactors is approximately 8 %. The conversion is related to the amount of the stoechiometric limiting reactant – butene in our case - thus, higher conversion levels in the laboratory reactor are not expected [2, 3].

The system we studied involves two reactions in series, the hydration of the butene to secondary butanol and the etherification of the secondary butanol to di-secondary-butyl-ether, with both reactions reversible. The reverse reaction –etherification- can be neglected for the hydration process carried on under the operation conditions corresponding to temperatures between 117 and 130°C, 60 bar pressure and the catalyst particle dimensions below 0.71 mm. By carring on the hydration under conditions presented above, no etherification reaction product was detected because the reaction was carried on in such way to avoid the formation of byproducts by placing the catalyst in the baskets located into the water phase, thus limiting the concentration of butene at the catalyst surface.

Taking into account that the butene hydration, under laboratory reactor conditions, is a multiphase reaction, and two liquid phases occur in the reactor, it is mandatory to write a suitable mass balance equation for this system.

Because in our experimental set up the effect of the adsorption of the reactants on the inner surface and chemical reaction on specific active sites cannot be separated; the cumulated effect of these steps will be studied together; therefore three 2-butanol concentration levels were used in these experiments: 5, 8 and 20 wt%. At the beginning, the reactor was filled with water-SBA mixtures and the operating pressure was set. The reactor was heated to the desired reaction temperature, between 117-130°C. After reaching the desired temperature, the butene was fed to the reactor, until the separation line between the phases reaches the middle of the reactor. After the volumetric butane to water ratio was set and corresponding volumetric flow rate was adjusted, the stirrer was started. The operating parameters are given in table 4.

Table 4
THE EXPERIMENTAL PARAMETERS FOR KINETIC INVESTIGATIONS

Temperature, °C	117, 120, 125, 130
Pressure, bar	60
Volumetric ratio Butene:Water	75:25, 80:20
SBA wt% in the feed	5, 8, 20
Space time, g_{cat}/mol/min	47
Catalyst weight, g	3
Stirring speed, RPM	800

After a certain time, long enough to reach the steady state (1 hour after temperature and pressure become constant), samples from the olefin phase were collected and analyzed by GC. The main product - secondary butanol - is the result of the chemical reaction between the adsorbed reactants on the active sites of the catalyst. After desorption, secondary butanol migrates into the water phase. The supercritical butene also extracts the secondary butanol and, for this reason, the alcohol will be distributed in both phases, mostly being concentrated in the olefin phase [11, 12]. For each set of operating parameters, at least three samples were analyzed, the mean value being used for the calculation of the reaction rates.

The observed reaction rate (r_{SBA}) was calculated with the equation (1).

$$r_{SBA} = \frac{F_{C_4} \cdot x_{SBA,C_4prod}}{W \cdot CAP} \qquad (1)$$

with

$$x_{SBA,C_4prod} = x_{SBA,C_4out} - x_{SBA,C_4in} \qquad (2)$$

where:

F_{C4} represents the molar flow rate of butene;

$x_{SBA,C4prod}$ - the molar fraction of SBA (produced in the hydration) located into the butene phase;

$x_{SBA,C4out}$; $x_{SBA,C4in}$ - the molar fraction of SBA in the butene phase from outlet and inlet.

Equation (2) gives the increase of SBA concentration (found in the organic phase) as result of chemical reaction. The SBA quantity produced is calculated as a difference between the SBA quantity in the outlet and the SBA quantity in the feed.

The reaction rates were calculated with equation (1), the numeric values could be found in the tables from 5 to 8. In figure 5 the steady state rates for 5wt % 2-butanol concentration level versus 1/T is given.

The reaction rate was found to increase with increasing temperature and with the decreasing of the volumetric butene to water ratio in the inlet. Low (1, 2 and 5 wt%) concentrations of secondary alcohol in the feed are beneficial for the process; secondary butanol acts as a cosolvent and improves the solubility of butene in water, consequently the apparent reaction rates increase [11].

Microkinetic model

The butene-water-2 butanol mixture under reaction conditions causes some difficulties in the prediction of the phase behavior due to the supercritical state of butene and also due to a very low mutual solubility between butene and water. More than that, water and 2-butanol are strongly

Table 5

THE EXPERIMENTAL PARAMETERS AND THE REACTION RATES IN SBA SYNTHESIS AT 117°C

Constant parameters		T= 117 °C, P=60 bar, 0.5<x<0.71, 800 RPM					
Mixtures SBA in water, wt%		5		8		20	
Volumetric ratio Butene:Water		75:25	80:20	75:25	80:20	75:25	80:20
Molar ratio Water:Butene		1.79:1	1.34:1	1.74:1	1.30:1	1.53:1	1.15:1
Catalyst weight, g		3					
Particle size of the catalyst, mm		0.50<x<0.71					
Capacity of the catalyst, eq/g		0.00152					
Space time, g cat/mole/min		47.06					
Feed ratio, ml/min		3.100	3.462	3.114	3.476	3.170	3.531
Butene feed ratio, mole/h		1.37	1.63	1.37	1.63	1.4	1.67
Water (+SBA) feed, mole/h		2.45	2.19	2.45	2.19	2.42	2.2
SBA, mol fr inlet		0.00811	0.00724	0.01313	0.01171	0.03461	0.03057
mol fr. outlet	SBA, mole fr,	0.0425	0.0227	0.0562	0.0380	0.2726	0.2234
	Water, mole fr,	0.0601	0.0523	0.0892	0.0424	0.0982	0.0854
	Butene, mole fr,	0.8972	0.9249	0.8541	0.9194	0.6288	0.6903
	Others (TBA), mole fr,	0.0002	0.0001	0.0005	0.0002	0.0004	0.0009
Reaction rate, mole/eq/h		10.33	5.53	12.99	9.43	73.12	70.4
Reaction rate, mole/eq/s $\cdot 10^3$		2.87	1.53	3.61	2.61	20.3	19.5

Table 6

THE EXPERIMENTAL PARAMETERS AND THE REACTION RATES IN SBA SYNTHESIS AT 120°C

Constant parameters		T= 120 °C, P=60 bar, 0.5<x<0.71, 800 RPM					
Mixtures SBA in water, wt%		5		8		20	
Volumetric ratio Butene:Water		75:25	80:20	75:25	80:20	75:25	80:20
Molar ratio Water:Butene		1.79:1	1.34:1	1.74:1	1.30:1	1.53:1	1.15:1
Catalyst weight, g		3					
Particle size of the catalyst, mm		0.50<x<0.71					
Capacity of the catalyst, eq/g		0.00152					
Space time, g cat/mole/min		47.06					
Feed ratio, ml/min		3.100	3.462	3.114	3.476	3.170	3.531
Butene feed ratio, mole/h		1.37	1.63	1.37	1.63	1.4	1.67
Water (+SBA) feed, mole/h		2.45	2.19	2.45	2.19	2.42	2.2
SBA, mole fr inlet		0.00811	0.00724	0.01313	0.01171	0.03461	0.03057
mol fr. outlet	SBA, mole fr,	0.0432	0.0252	0.0571	0.0422	0.2270	0.1827
	Water, mole fr,	0.0665	0.0839	0.0669	0.0726	0.0558	0.0567
	Butene, mole fr,	0.8899	0.8905	0.8757	0.8848	0.7168	0.7603
	Others (TBA), mole fr,	0.0004	0.0004	0.0003	0.0004	0.0004	0.0003
Reaction rate, mole/eq/h $\cdot 10^3$		10.54	6.43	13.26	10.93	59.1	55.5

polar species and form an azeotrop with maximum temperature.

The operating conditions for the hydration of butene were chosen to correspond to the supercritical butene. The liquid-liquid equilibrium (LLE) is of essential importance in this work, since the reaction between water and butene is operated under such conditions that a homogeneous region is expected therefore, LLE must be investigated for a complete overview of the phase equilibrium.

Because of the problems presented above, only modified cubic equation of state as the Predictive Soave-Redlich-Kwong (PSRK), which incorporate temperature-dependent terms, together with UNIQUAC are reliable to predict the real behavior of high non-ideal mixture with polar compounds such our multicomponent fluid mixture.

Based on equilibrium composition (the composition of both liquid phases in equilibrium at 160°C was measured

Table 7

THE EXPERIMENTAL PARAMETERS AND THE REACTION RATES IN SBA SYNTHESIS AT 125°C

Constant parameters		T=125 °C, P=60 bar, 0.5<x<0.71, 800 RPM					
Mixtures SBA in water, wt%		5		8		20	
Volumetric ratio Butene:Water		75:25	80:20	75:25	80:20	75:25	80:20
Molar ratio Water:Butene		1.79:1	1.34:1	1.74:1	1.03:1	1.53:1	1.15:1
Catalyst weight, g		3					
Particle size of the catalyst, mm		0.50<x<0.71					
Capacity of the catalyst, eq/g		0.00152					
Space time, g cat/mole/min		47.06					
Feed ratio, ml/min		3.100	3.462	3.114	3.476	3.170	3.531
Butene feed ratio, mole/h		1.37	1.63	1.37	1.63	1.4	1.67
Water (+SBA) feed, mole/h		2.45	2.19	2.45	2.19	2.42	2.2
SBA, mole fr inlet		0.00811	0.00724	0.01313	0.01171	0.03461	0.03057
mol fr. outlet	SBA, mole fr,	0.0456	0.0284	0.0602	0.0473	0.1719	0.1361
	Water, mole fr,	0.0665	0.0604	0.0801	0.0567	0.0509	0.0381
	Butene, mole fr,	0.8875	0.9110	0.8593	0.8956	0.7767	0.8254
	Others (TBA), mole fr,	0.0004	0.0002	0.0004	0.0004	0.0004	0.0004
Reaction rate, mol/eq/h $\cdot 10^3$		11.3	7.57	14.20	12.74	42.2	38.52

Table 8

THE EXPERIMENTAL PARAMETERS AND THE REACTION RATES IN SBA SYNTHESIS AT 130°C

Constant parameters		T= 130 °C, P=60 bar, 0.5<x<0.71, 800 RPM					
Mixtures SBA in water, wt%		5		8		20	
Volumetric ratio Butene:Water		75:25	80:20	75:25	80:20	75:25	80:20
Molar ratio Water:Butene		1.79:1	1.34:1	1.74:1	1.03:1	1.53:1	1.15:1
Catalyst weight, g		3					
Particle size of the catalyst, mm		0.50<x<0.71					
Capacity of the catalyst, eq/g		0.00152					
Space time, g cat/mole/min		47.06					
Feed ratio, ml/min		3.100	3.462	3.114	3.476	3.170	3.531
Butene feed ratio, mole/h		1.37	1.63	1.37	1.63	1.4	1.67
Water (+SBA) feed, mole/h		2.45	2.19	2.45	2.19	2.42	2.2
SBA, mole fr inlet		0.00811	0.00724	0.01313	0.01171	0.03461	0.03057
mol fr. outlet	SBA, mole fr,	0.0474	0.0319	0.0627	0.0529	0.1351	0.1171
	Water, mole fr,	0.0660	0.0601	0.1244	0.0466	0.0389	0.0351
	Butene, mole fr,	0.8864	0.9080	0.8122	0.8998	0.8255	0.8474
	Others (TBA), mole fr,	0.0002	0.0000	0.0007	0.0007	0.0005	0.0004
Reaction rate, mole/eq/h $\cdot 10^3$		11.8	8.83	14.96	14.77	30.87	31.58

by LTP Oldenburg) at a certain temperature and with help of PSRK equation of state and UNIQUAC it was possible to predict the thermodynamic behaviour of the multicomponent system at different temperatures as well as the calculation of fugacities corresponding to the butene phase [10, 12].

The general condition for two phases to be in thermodynamic equilibrium can be described in terms of fugacity with the equation (3).

$$f_i^{'} = f_i^{''} \qquad (3)$$

Langmuir-Hinshelwood isotherms are assumed for describing the sorption behaviour of the components of the reaction mixture (1-butene, water and secondary butanol) in the catalytic active gel phase of the resin [13, 18]. Therefore the sorption equilibria of 1-butene, water and secondary butanol on one active site **s** is given by the equations (4-6) and the fraction of the actives sites

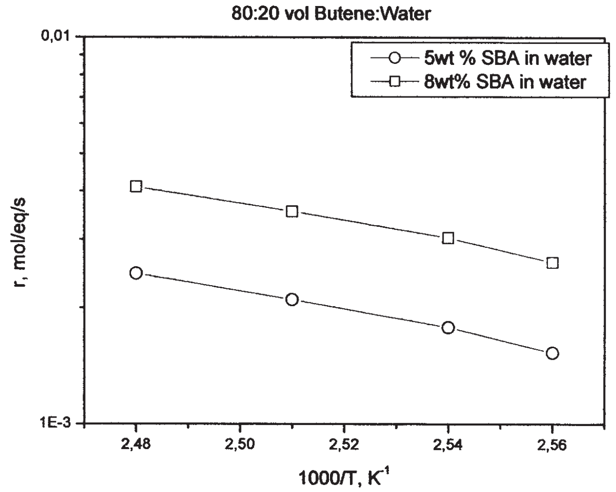


Fig. 5. Observed reaction rate, r_i, of the butene hydration reaction versus 1/T [10]

occupied by component **i** can be written as equation (7) with the observation that the liquid phase concentration of the species **i** (C_i) can be replaced by the activities a_i ($a_i = x_i \cdot y_i$) or by the fugacities f_i ($f_i = p \cdot \varphi_i \cdot x_i$). Since our reaction system is strongly nonideal and the operating pressure is very high, the behaviour of this system can be better described in terms of fugacities.

$$butene + s \xleftrightarrow{k_{+b},k_{-b}} butene \bullet s \tag{4}$$

$$water + s \xleftrightarrow{k_{+w},k_{-w}} water \bullet s \tag{5}$$

$$SBA + s \xleftrightarrow{k_{+a},k_{-a}} SBA \bullet s \tag{6}$$

$$\theta_i = K_i \cdot \theta_v \cdot C_i = \frac{K_i \cdot C_i}{1 + \sum_{i=1}^{N} K_i \cdot C_i} \tag{7}$$

Due of this reason the fraction of the active sites occupied by the component **i** and the reaction rate equation are formulated in terms of fugacities.

$$\theta_i = K_i \cdot \theta_v \cdot f_i = \frac{K_i \cdot f_i}{1 + \sum_{i=1}^{N} K_i \cdot f_i} \tag{8}$$

The rate-determining step, the chemical reaction of sorbed molecules, was formulated according to the homogeneous catalysis as first order in all species (as it is presented in equation 10) [16, 17].

$$butene \bullet s + water \bullet s \xleftrightarrow{k_1,k_{-1}} SBA \bullet s + s \tag{9}$$

$$r_b = k_{-1} \cdot \theta_a \cdot \theta_v - k_1 \cdot \theta_b \cdot \theta_w \tag{10}$$

According to the equation (9) and (10) the rate of the chemical reaction can be written as:

$$\theta_i = K_i \cdot \theta_v \cdot f_i = \frac{K_i \cdot f_i}{1 + \sum_{i=1}^{N} K_i \cdot f_i} \tag{11}$$

$$r = k_1 \cdot \theta_b \cdot \theta_w - k_{-1} \cdot \theta_a \cdot \theta_v \tag{12}$$

Inserting equation (11) into equation (12) leads to an expression for the reaction rate, where the fractions of occupied sites are controlled by the fugacities of the components:

$$r = \frac{k_1 \cdot K_b \cdot K_w \cdot f_b \cdot f_w - k_{-1} \cdot K_a \cdot f_a}{\left(1 + \sum_{i=1}^{N} K_i \cdot f_i\right)^2} \tag{13}$$

The kinetics for the forward reaction between butene and water was very well described by a model equation with four adjustable parameters based on Langmuir-Hinshelwood kinetics.

As previously described, two liquid phases occur during the direct hydration of liquid butene in the laboratory reactor. The main product, the secondary butanol, is formed in the water phase and it is extracted by supercritical butene into the organic phase. Due to the bigger quantity of the main product concentrated into the organic phase, the fugacities are related to this phase.

The expression for the reaction rate equation that fit our experimental results is given bellow.

$$r = \frac{k_1 \cdot K_b \cdot K_w \cdot f_b \cdot f_w}{\left(1 + K_b \cdot f_b + K_w \cdot f_w\right)^2} \tag{14}$$

with:

$$k_1 = k_0 \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \tag{15}$$

The calculated values for the kinetic parameters, K_b and K_w are given in table 9.

The Arrhenius equations (15) together with Arrhenius plot (fig. 6) were used for the calculation of the Arrhenius parameters (E_a and k_0).

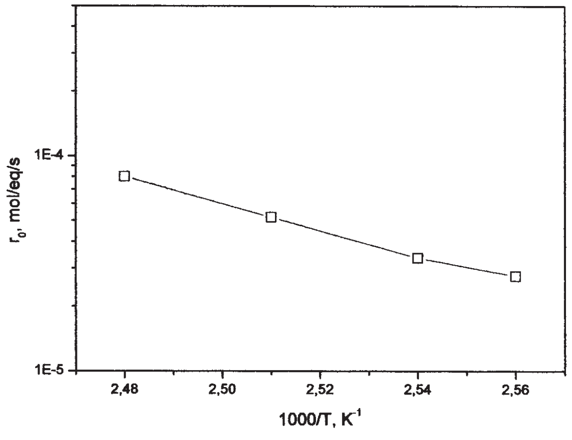


Fig. 6. Observed reaction rates as function of temperature

The activation energy calculated for the butene hydration on Amberlyst DT, in temperature range of 117-130°C is about 110 kJ/mole and the preexponential factor k_0 is 1.14 mole/eq/s.

In order to correlate our experimental data with the reaction rate equation proposed (14), we used a powerful simulation program (MathLab). For MathLab simulations we utilized the activation energy resulting from calculations, respectively 110 kJ/mole, while the preexponential factor was fitted.

The value for the preexponential factor obtained after simulation in MathLab, which verify the expression of the reaction rate proposed, was found to be 1.466 mole/eq/s.

Table 9
MODEL PARAMETERS FOR EQUATION (14)

Parameter	Unit	Value
k_0	mole/eq/s	$1.466\ 10^{11}$
K_b	l/bar	0.038
K_w	l/bar	1.075
E_a	kJ/mole	110.16

The objective function F(x) calculated with equation (16) is 5 . 7 . 10^{-03}, suggesting a very good agreement between the rate expression and the experimental data.

$$F(x)=\sum\left|\frac{r_{i,\exp}-r_{i,cal}}{r_{i,\exp}}\right|^2=5.7\cdot10^{-03} \quad (16)$$

The model parameters for equation 14 are shown in table 9.

Conclusions

Since reliable kinetic data are only obtained in a domain unaffected by transport phenomena preliminary experiments were done to check the influence of the film diffusion and the internal mass transfer. It was found that for stirring speeds higher than 800 RPM we are in a domain free of external diffusion and for the catalyst particle dimensions below 0.71 mm and temperature range 117 to 130°C the effect of the internal diffusion can be neglected. Therefore, the kinetic investigations were done under conditions previously presented.

Based on our experimental data we propose an expression for the rate equation of the forward reaction between butene and water described by a model equation with four adjustable parameters based on Langmuir-Hinshelwood kinetics expressed in terms of fugacities.

The expression of the rate equation proposed fits very well the experimental data and results in apparent activation energy value consistent with those reported by other authors. The MathLab simulations performed in order to correlate our experimental data with the reaction rate equation proposed, lead to a value for preexponential factor similar with that calculated based on the Arrhenius equation and Arrhenius plot.

List of notations

Symbol	*Unity*	*Meaning*
a	[-]	activity
f	[bar]	fugacity
k	[s^{-1}]	reaction rate constant
k_0	[s^{-1}]	Arrhenius parameter
r	[mol/eq/h][-]	reaction rate
x	[-]	molar fraction
C	[mol/l]	liquid phase concentration
CAP	[eq/g]	catalyst capacity
E_a	[J/mol/K]	activation energy
F	[mol/min]	molar flow
K	[-]	adsorption rate constant
R	[dmłbar/mol/K]	general gas constant
T	[K]	absolute temperature
W	[g]	catalyst weight
φ	[-]	fugacity coefficient
γ	[-]	activity coefficient
Θ_i	[-]	fraction of actives sites occupied by component i
Θ_v	[-]	fraction of vacant sites

Indices

cal	calculated
exp	experimental
in	inlet
out	outlet
C_4	butene phase
1	direct reaction
-1	reverse reaction
a	alcohol
b	butene

Abbreviationx

SBA	Secondary butanol
RPM	Rotation per minute

References

1. BOHÎLŢEA, I., Reactoare chimice, Universitatea Petrol-Gaze Poieşti, Romania, 1996,
2. *** BP CHEMICALS, German patent, 1972, 2 340 816
3.*** DEUTSCHE TEXACO AKTIENGESELLSCHAFT CHEMIE, “Development of a process for direct hydration of n-butenes basis Isopropanol process Know How. Kinetic studies in the batch reactor”, 1978, report no. 10
4. DOUGLAS, W.J.M., “Hydration of n-butene with cation exchange resins”, PhD Thesis, University of Michigan, 1958, USA
5. FOGLER, H.S., “Elements of chemical reaction engineering”, 1999, Prentice-Hall International, 3rd edition
6. HELFFERICH, F., “Ion Exchange”, 1962, McGraw-Hill, New York
7. KUNZ, U., Versatile pulse-width-modulator, 1991, Elektor Electronics, 5, 48
8. KUNZ, U., HOFFMANN, U., Design of a high pressure liquid/liquid/solid catalyst reactor, work report, 2003, TU Clausthal, ICVT, Germany
9. LEVENSPIEL, O., „Chemical reaction engineering”, 1999, Wiley& Sons, New York
10. PETRE, D., Kinetic investigations on direct hydration of n-butenes in a multiphase reactor, 2006, PhD Thesis, TU Clausthal, germany
11. PETRE, D.,Rev. Chim. (Bucharest), **58**, no. 8, 2007, p. 833
12. PETRE, D., „An inferential method for VLLE prediction- application for n-butene-water-secondary butanol mixtures”, 2006, Buletinul UPG Ploiesti, LVIII, 2006, p. 213
13. PETRUS, L., „Hydration of lower alkenes catalyzed by strong acid ion exchangers”, 1982, PhD Thesis, University of Groningen, The Netherlands
14. PFEUFFER, B., Verbesserung des Analysesystems und kinetische Untersuchungen zur heterogenkatalytischen Direkthydratisierung von n-Butenen, 2005, Diplomarbeit, TU Clausthal, Germany
15. REHFINGER, A., „Reaktionstechnische Untersuchungen zur Flüssigphasesynthese von Methyl-tert.-butylether (MTBE) an einem starksauren makroporösen Ionenaustauscherharz als Katalysator”, 1988, PhD Thesis, TU Clausthal, Germany
16. REHFINGER, A., HOFFMANN, U., „Kinetics of methyl tertiary butyl ether liquid phase synthesis catalyzed by ion exchange resin. Intrinsic rate expression in liquid phase activities”, Chemical Engineering Science, 45, 6, 1990, p. 1605
17. REHFINGER, A., HOFFMANN, U., “Kinetics of methyl tertiary butyl ether liquid phase synthesis catalyzed by ion exchange resin. Macropores diffusion of methanol as rate controlling step”,Chemical Engineering Science, 45, 6, 1990, p. 1619
18. REHFINGER, A., “Reaktionstechnische Untersuchungen zur Flüssigphase-synthese von Methyl-tert.-butylether (MTBE) an einem starksauren makroporösen Ionenaustauscherharz”, PhD Thesis, TU Clausthal, 1988, Germany
19. RICHON, D., Procede et dispositif pour prelever des micro-echantillons d’un fluide sous pression contenu dans un container, 2003, EP 1105722 B1
20. SAJDOK, J., Entwurf eines Reaktors für die heterogen-katalytische Direkthydratisierung von n-Butenen zu 2-Butanol, 2004, Studienarbeit, TU Clausthal, Germany

Manuscript received: 3.11.2009