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DEVELOPMENT OF A MODULAR MICROREACTOR FOR THE PARTIAL HYDROCARBON OXIDATION.

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DEVELOPMENT OF A MODULAR MICROREACTOR FOR THE PARTIAL HYDROCARBON OXIDATION.

The industrially important partial oxidation of hydrocarbons is frequently characterized by low conversions and yields, which are mostly related to mass and heat transfer problems. Due to the reaction conditions, such processes include also important safety risks and are still not sufficiently investigated. To study the influence of the process parameters on the product selectivity, a lab facility including a silicon-coated micro reactor of stainless steel has been developed and constructed. Due to its modular construction (e.g. replaceable capillary), it permits for the first time to perform catalyzed and non-catalyzed oxidations of hydrocarbons with oxygen as a two-phase process in a capillary reactor in a wide range of residence times (some mins to 24 h), temperatures and pressures. Especially wide ranges of reactant ratios and concentrations of inert gas, initiator and additive are also accessible. The challenges of the reactor construction and their solutions are discussed.

Keywords: Micro reactor, process intensification, isobutane, hydrocarbon oxidation, t-butyl hydroperoxide, multiphase flow.

1 Introduction

The partial oxidation of alkanes and aromates is an important industrial process type for the production of chemical mass products and fine chemicals. Beside basic chemical products like phenol, dicarbon acids (e.g. adipic acid, maleic acid, succinic acid), alcohols (secondary paraffin alcohols), ketones (e.g. acetone) and fine chemicals such as hydroperoxides (t-butyl hydroperoxide (TBHP), cumene hydroperoxide) and hydroxy aromates (e.g. resorcin, hydroquinone) are produced by oxidation of hydrocarbons (Arpe, 2007). Such processes are often produced at low conversions and yields, which are mostly related to mass and heat transfer problems (Hessel, Gursel, Wang, Noel, & Lang, 2012). Also, due to the process conditions (high temperatures and pressures, air or pure oxygen and hydrocarbons) such industrial processes performed in batch mode already caused several accidents (Høiset, Hjertager, Solberg, & Malo, 2000), since they include important safety risks. They require special safety equipment (e.g. high pressure bunker, remote control rooms). The investigation of processes including the oxidation of hydrocarbons is therefore especially challenging and the related experiments are often not feasible in a laboratory. Such problems contribute to the fact that oxidation processes are nowadays still not sufficiently investigated (Gemoets et al., 2016).

Many different special oxidation reactor designs (e.g. (Bjerrum, Xiao, & Hjuler, 2002; Braithwaite, Bryant, Miller, & Logsdon, 2002; Greene, Sumner, & Gartside, 1998; Kingsley & Roby, 1996; Langley & Tulip, 1977; Ramachandran & Balaraman, 2004; Shirley & Ramachandran, 1996)) have been published. To give the principal idea, the so-called liquid oxidation reactor (LOR reactor (Roby & Kingsley, 1996)) shall be described shortly. It has been utilized in several partial oxidation patents (e.g. cyclohexane (Greene et al., 1998), xylene (Kingsley & Roby, 1996)). Pure oxygen could not be used for the hydrocarbon oxidation in a conventional reactor, since it

would be necessary to dilute it in the gas phase with nitrogen below the flammability limit which makes such a process unattractive. By feeding and keeping the oxygen bubbles directly in the liquid hydrocarbon phase below the surface, the LOR is capable of improving significantly the reaction of oxygen and hydrocarbon and hence achieving a better energy efficiency, gas utilization and higher oxidation rates than conventional reactors. The recirculation of oxygen bubbles is accomplished by a downward axial flow impeller contained within a draft tube and a gas containment baffle (Roby & Kingsley, 1996). The oxygen concentration in the gas phase is maintained at 5 %. However, such reactors do neither solve the problem of the undefined interface area nor the heat transfer problems of conventional reactors. Although the security is enhanced, such a reactor cannot be considered as inherently safe.

Because of the worldwide energy situation, the energy efficiency of all kinds of processes needs to be reviewed. Current research on chemical reaction processes is focusing on the intensification of processes by miniaturization of the equipment with the aim to overcome e.g. mass and energy transport limitations in the case of multiphase reactions. A micro structured reactor, e.g. micro capillary reactor, has favorable properties to realize these goals due to its high ratio of surface to volume. This prevents the formation of hot spots in the reaction mixture and allows often obtaining higher selectivities of the desired products. Furthermore, micro reactors – although not inherently safe (Hieronymus et al., 2011a) – are much safer than batch reactors and thus allow the exploration of new process windows e.g. within the explosive range.

As discussed by Schwesinger (Schwesinger, 2000), the flexibility of modular micro reactors compared to conventional constructions is an important advantage. The design of modular reactors has been already published in connection with several types of multiphase flow reactions, e.g. the oxidation of glucose with glucose oxidase and

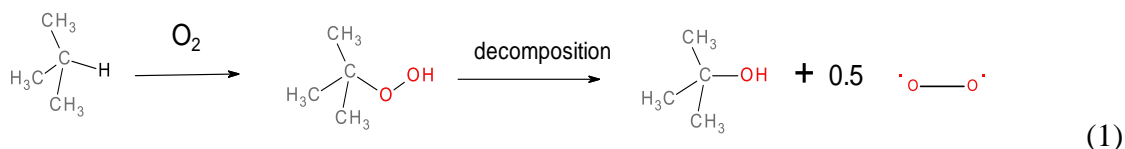
oxygen (Viefhues et al., 2017), the carbonylation of benzaldehyde and acetaldehyde to 2-hydroxy propiophenon by benzoylformate decarboxylase (Fagaschewski, Bohne, Kaufhold, Mueller, & Hilterhaus, 2012)), the precipitation of calcium carbonate from calcium hydroxide and carbon dioxide (Kurt, Akhtar, Nigam, & Kockmann, 2016), the production of organic nitrates (Braune et al., 2009), the heterogeneously catalysed esterification of higher alcohols (Kulkarni, Zeyer, Jacobs, Kaspereit, & Kienle, 2008) and the catalytic selective oxidation of ammonia and propene (Beato, Kraehnert, Engelschalt, Frank, & Schloegl, 2008). The Fraunhofer Alliance Modular Micro Reaction System (FAMOS) which enables an arrangement of all micro devices on one platform on the basis of ceramic components to perform catalytic reactions needs also be mentioned (Moritz, Lenk, Adler, & Zins, 2005) in this context. Furthermore, a modern tendency is also the lab on a chip where similar concepts are used for catalytic reactions (Blankenstein & Larsen, 1998)(Knitter & Liauw, 2004). However, despite the favorable properties of the presented micro devices, long residence times of up to 24 h or more as they are necessary for the investigation of many radical reactions like the oxidation of cumene, isobutane, p-xylene etc. (Arpe, 2007) cannot be realised with such systems since neither a sufficient reactor length can be set nor a sufficiently low volume flow of the components established.

Therefore, a modular lab facility with a micro reactor has been developed, constructed and tested to investigate the partial oxidation of hydrocarbons as a two-phase process in a broad range of flow rates, temperatures ($T = 75$ to 165 °C) and pressures ($P = 25$ to 100 bar). For the sake of convenience, an exchangeable capillary of a variable length (100 m in the present state) and an inner diameter (ID) of 1 mm has been used instead of a monolith reactor. Micro reactors are sufficiently safe to perform experiments in the explosive range of gas mixtures, if the volume of the entire lab

facility (sampling unit, blow-down vessel) is kept small and precautions concerning a pressure or temperature increase due to a run-away reaction are taken. Furthermore, the formation of electrical charges and sparks, respectively and of a detonatable mixture of the hydrocarbon and oxygen need to be prevented. The modular construction allows for any operation conditions of the micro reactor by introducing the corresponding modifications. Due to the numerous unexpected challenges we encountered during the construction of this micro reactor, it was decided to make the solutions found available to other researchers. Therefore, in the present work the construction of the micro reactor has been illustrated, proving the functionality by performing the oxidation of isobutane with oxygen at two phase flow conditions as an example process.

2 General considerations on the isobutane oxidation

The production of TBHP by oxidation of liquid isobutane is an example for the partial oxidation of hydrocarbons. TBHP is used for numerous applications as for industrial polymerizations and oxidations as well as in organic synthesis. It becomes more and more important since the hydroperoxide is used to oxidise propylene to propylene oxide in the frame of the oxirane process. Propylene oxide is an important product for the manufacturing of polymers, anti-freezing products etc. However, the production process of TBHP by the non-catalysed oxidation of isobutane has still a big potential of improvement. The reaction is currently conducted in bubble-cap tray reactors and bubble columns at 120 - 140 °C and 25 - 35 bar with a selectivity of about 60 mole% at a conversion of 45 mole% (Arpe, 2007). It is quite exothermic with a reaction enthalpy of -100 to -250 kJ/ mole. An extremely simplified reaction scheme of this reaction is given by eq.1.



The reaction proceeds via a radical mechanism, which is complicated by the formation of decomposition products of TBHP and their oxidation products conducting to formic acid, carbon monoxide and carbon dioxide. The decomposition of TBHP produces further radicals, which induce further decomposition reactions and make the reaction autocatalytic. A quite realistic reaction scheme would comprise between 12 and 20 elementary reactions (Allara, Edelson, & Irwin, 1972). A critical literature research considering about 200 scientific papers revealed that no model has been created yet that was applicable within the interesting experimental pressure, temperature and concentration ranges.

There are few investigations on the non-catalytic partial oxidation of isobutane at low temperature yet (Allara et al., 1972; Allara, Mill, Hendry, & Mayo, 1968; Hieronymus et al., 2011b; Mistrik & Kostal, 1977; Nangia & Benson, 1980; Shah, Mahajani, Sharma, & Sridhar, 2000; Shah, 1998; Suresh, 1998; Winkler & Hearne, 1961). Among those, only Shah (Shah et al., 2000; Shah, 1998) investigated the reaction of isobutane in a micro reactor. Shah used a stainless steel tube of about 12 m length with glass coated walls (1 mm thickness) and an inner diameter of 2 mm. He performed a single phase reaction by saturating isobutane with oxygen (< 6.1 mole%) and reached only very small conversions ($\leq 0.61\%$). On the basis of the autocatalytic effect of the hydroperoxide formed, the kinetic rate r (Eq. (2)) of the isobutane oxidation as an autocatalytic reaction with the temperature dependent reaction rate constant $k(T)$ and the conversion U has been derived.

$$r = k(T) \cdot (1 - U) \cdot U \cdot [iC_4H_{10}]^2 \quad (2)$$

Shah et al. (Shah et al., 2000), who also derived this formula, determined $k(T)$ on the basis of literature data at very low conversion degrees ($< 2\%$). Using this formula and the velocity constants of Shah (Shah et al., 2000), the conversion of isobutane U_{IB} has been derived as a function of temperature T and reaction time t_1 (Eq. (3)).

$$U_{IB}(T, t_1) = \left(1 + \left(\frac{1 - U_{IB,0}}{U_{IB,0}}\right) \cdot \exp(-k'(T) \cdot C_{IB,0} \cdot t_1)\right)^{-1} \quad (3)$$

with $k'(T) = k(T) \cdot [O_2]$, $C_{IB,0}$: initial concentration of isobutane, $U_{IB,0}$: initial conversion, exp: exponential function

Figure 1 shows the resulting theoretical conversion curves estimated by this formula for different temperatures, irrespective of the restricted conversion validity range of the model.

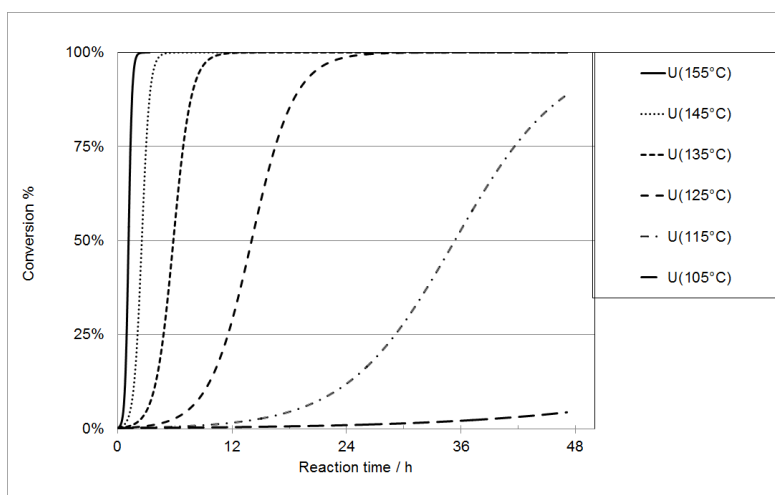


Figure 1. The conversion curves of the hydrocarbon as a function of time at different temperatures for the oxidation of isobutane as an example process..

Due to the complex reaction mechanism, the conversion of isobutane is, of course, not equal to the formation of the hydroperoxide - especially at higher temperatures -, but there is no known direct relation. The formation of TBHP depends on the conversion of isobutane, but the decomposition of TBHP according to Eq. (1) depends on temperature, its own concentration and the concentrations of its

decomposition products. Therefore, the reaction can only be simulated by the application of complex reaction schemes.

3 Reactor design

3.1 Functionality

The lab-scale plant had to be designed as a continuously operating micro reactor. A number of requirements were established for its design. All tubes including the reactor itself should be in the range of 1 mm inner diameter to minimize the volume of the construction as well as to assure an optimal heat removal. It should give the possibility to feed the hydrocarbon, oxygen, nitrogen, a noble gas, an additive and an initiator solution at low mass flows and within a wide range of temperatures and pressures (Table 1) using mass flow controllers and/or pumps. Possible initiators should include TBHP, di-t-butyl peroxide (DTBP), hydrogen peroxide as well as other peroxy compounds (peresters). Furthermore, the liquids need to be conducted together at the desired pressure and later unified with the gas stream by a T-junction using a hollow needle for the gas introduction. Then, the entire stream is passed through a steel capillary reactor, which will be set to the desired temperature. The gas-liquid flow should be a Taylor-Flow with a minimum of pressure pulsation and disturbances. Therefore, it should be possible to use a capillary made of glass instead steel to investigate the Taylor flow characteristics by photographs.

There were two product vessels, one for the continuous flow until the steady state is achieved (waste) and one for sampling. By means of a three-way-valve it could be controlled into which vessel the flow was conveyed. During the sampling period, the liquid hydrocarbon phase - containing liquid reaction products - and gaseous products were separated in the sampling part else they were separated in the waste container. To

achieve a constant reaction pressure without pulsation, the whole system pressure was determined and regulated by the pressure of the gas phase using a valve combined with a pressure sensor. Since the reaction mixture of the process was thermally unstable, the flow needed to be cooled down in a heat exchanger directly after the capillary to prevent further reactions and collected in a cooled pressure vessel containing a quenching liquid. Then the sample has to be analyzed by gas chromatography-mass spectrometry (GC-MS) under ambient temperature and pressure. A P&ID scheme is given in Figure 2.

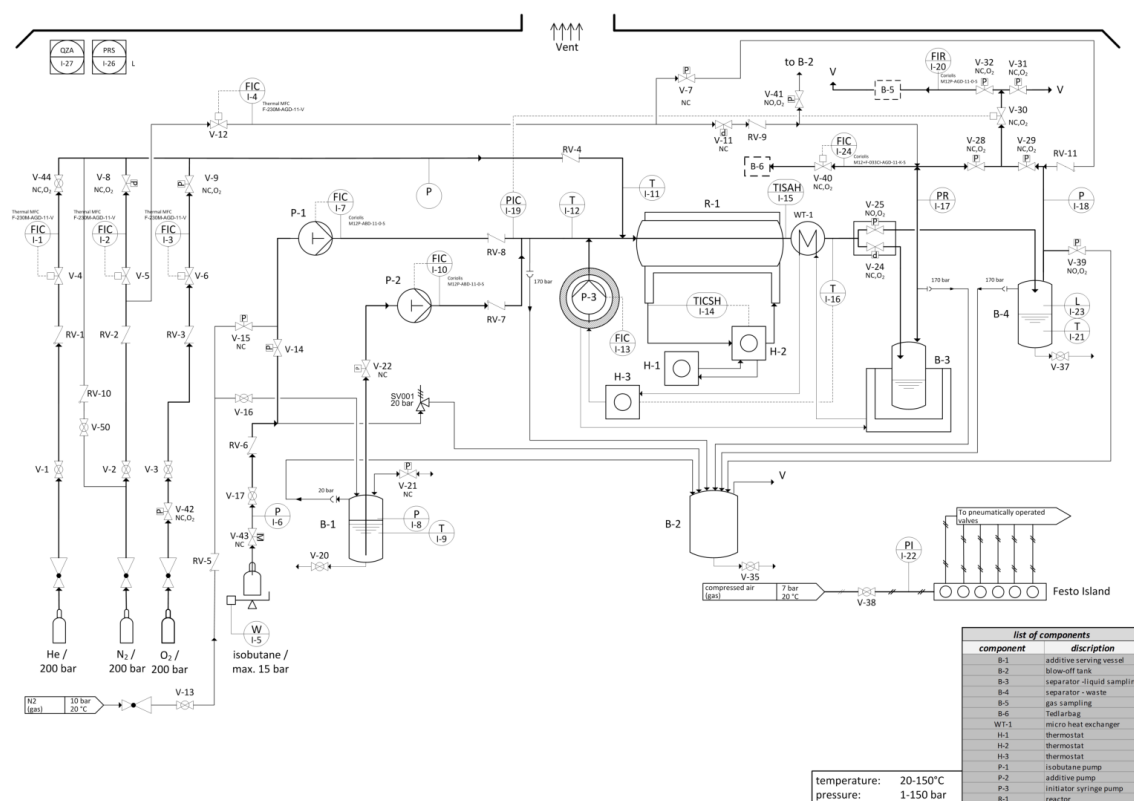


Figure 2. P&ID scheme of the modular micro reactor facility.

Finally, the lab facility needed a consistent, robust safety concept. It was planned to be controlled by a measurement and control technology software based on LabVIEW of National instruments, including a Real-Time system and a Fast Programmable Array (FPGA) module to ensure safety by low delay times of the safety devices in case of an increase of temperature or pressure.

3.2 Preliminary calculations

On the basis of the published kinetic results and different selected reactor lengths, the residence times as well as the gas and liquid flow rates to realize by the pumps and mass flow controllers have been calculated for the isobutane oxidation as a first example process at different mole ratios of the starting products, pressures and temperatures on the basis of general thermodynamic formulas (Table 1). For the conversion of mass flows into volume flows, the densities of all compounds, especially those of isobutane, have been obtained from the NIST data base (Witzgall, 1988) for all relevant pressure and temperature combinations. The two-phase volume flow, calculated by the reactor volume and the residence time has been split into the constituting liquid and gaseous sub flows by use of the molar ratio of the corresponding component relative to the isobutane flow as a basis. Some results of these calculations for the different starting products and reactor length are given in Table 1, which shows that the corresponding flows are often below 1 $\mu\text{L}/\text{min}$ and that a variable reactor length is needed to achieve the targeted residence times at acceptable flow rates.

Table 1. Effect of the residence time and reactor length on the volume flows of isobutane, oxygen, nitrogen, additive and initiator at operation conditions with reactor diameter of ID = 1 mm, initiator concentration of 0.5 mole%, molar ratio (N_2/O_2) = 4; and operation conditions P = 35 bar, T = 403.15 K.

Residence time (h)	Reactor length (m)	Flow velocity (cm/s)	Volume flow ($\mu\text{l}/\text{min}$)					
			Total	Isobutane	Oxygen	Nitrogen	Additive	Initiator
4	10	0.069	33	3.40	4.712	24	0.755	0.061

	20	0.139	65	6.80	9.424	48	1.511	0.122
	40	0.278	131	13.6	18.85	95	3.022	0.244
	80	0.556	262	27.2	37.70	190	6.043	0.488
	100	0.694	327	34.0	47.12	238	7.554	0.610
8	10	0.035	16	1.70	2.356	12	0.378	0.031
	20	0.069	33	3.40	4.712	24	0.755	0.061
	40	0.139	65	6.80	9.424	48	1.511	0.122
	80	0.278	131	13.6	18.85	95	3.022	0.244
	100	0.347	164	17.0	23.56	119	3.777	0.305
12	10	0.023	11	1.13	1.571	8	0.252	0.020
	20	0.046	22	2.27	3.141	16	0.504	0.041
	40	0.093	44	4.53	6.283	32	1.007	0.081
	80	0.185	87	9.07	12.57	63	2.014	0.163
	100	0.232	109	11.3	15.71	79	2.518	0.203

3.3 Design challenges

In contrast to normal liquid solvents, isobutane as a liquefied gas has some properties which complicated its handling. Due to its low viscosity and density, the most important problem was the limited availability of pumps, which are able to pump isobutane as a liquefied gas at elevated pressure and above its boiling point (b.p.: -11.8

°C at 1 bar). Neither the available peristaltic nor gear pumps were suitable for this, only HPLC pumps. However, other authors (Shah, 1998) (Witzgall, 1988), pumping isobutane at low temperatures (-30 °C) under its vapor pressure by an HPLC pump, were not able to get a constant and reproducible isobutane flow with high precision and an acceptable low flow pulsation. Therefore, if the liquefied gas was cooled and only under its vapor pressure (about 5 bars at 25 °C) the aspiration by a High Pressure Liquid Chromatography (HPLC) pump (piston pump) at a temperature of about 25 °C seemed to cause local vaporization and cavitation. On the basis of these observations (Shah, 1998) (Witzgall, 1988) we concluded that it was not possible to pump a liquid or a liquefied gas at a temperature of about 20 K below the boiling point by an HPLC pump. Some experiments to pump isopentane (b.p.: 27 °C at 1 bar) by an HPLC pump at room temperature (23 °C) also showed that, even if there is no problem visible on the aspiration side, there are still appearing bubbles in the transported liquid on the pressure side. Using hexane (b.p.: 68 °C) such a phenomenon has not been observed. This problem was solved by pumping liquefied isobutane under the pressure of 8 bars helium. The use of helium compared to nitrogen was favorable due to its lower solubility in most liquids. The isobutane was taken from a gas bottle with a riser pipe. As the density of liquefied isobutane depends on the pressure to a large extent, a constant mass flow could only be realized by a calibrated mass flow controller.

The wide ranges of mass flows and residence times to be realized were an important challenge for the experimental set-up. In principle the residence times can be easily adapted by varying the length of the micro reactor so that the experimental facility was suitable to investigate a variety of partial oxidation processes at different residence times. However, in the special case of isobutane, it was known that in the worst case, long residence times of up to 12 h or more had to be expected, because these

are required in an industrial environment and had been more or less confirmed by literature data (Shah et al., 2000). On the other hand, the goal was to increase the conversion at lower residence times (4 h) to enhance productivity and the large range of residence times should be realized using only one reactor length to reduce structural alteration works. Therefore, the residence times to be realized for isobutane were in the range of 4 to at least 12 hours. Even using a very long reactor capillary of 100 m length, the high residence times still required very small total flow rates in the reactor. As a result of the pressure, temperature and concentration ranges to be investigated, for both, gas flows and liquid flows, a wide range of flow rates from about some $\mu\text{L}/\text{h}$ to some mL/h needed to be realized for the different components.

For the pumping of isobutane and additives, mass flow controlled piston dosing pumps WADOSE-2-SS-U-S from Wagner Mess- und Regeltechnik GmbH (P-1 & P-2 in Fig. 2) have been used, which are coupled with Coriolis flowmeters (MiniCoriFlow, M12P-AGD-11-O-S, I-7 & I-10 in Fig. 2). The configuration allowed different operation modes (e.g. pressure, volume or mass flow controlled) and was capable to realize mass flows of 250 to 10,000 mg/h for isobutane and 1.2 to 60 g/h for an additive.

A special pump was needed for the initiator as the minimum concentrations were in the range of 0.125 mole%, corresponding to a flow in the order of about 15 mg/h, depending on the exact reaction conditions. Adding a solvent to dilute the initiator may lead to undesired side reactions destroying the initiator or the product. Consequently, it was decided to add a small volume flow of the pure initiator to the main flow of isobutane immediately before the reactor inflow. An 8 mL high pressure PHD ULTRA 4400 (HUGO SACHS) syringe pump (P-3 in Fig. 2) has been used, capable to pump a volume flow of 0.78 $\mu\text{L}/\text{h}$ to 3,500 $\mu\text{L}/\text{h}$ against 100 bars.

The small quantity of the initiator, which needed to be introduced into the reactor, brought about another challenge. A sufficient flow velocity was necessary at the injection point to ensure that the initiator was well distributed and present in each liquid plug of the Taylor-flow. Therefore, a glass capillary with an inner diameter of 20 μm , as it was available for chromatographic purposes, has been used to introduce the initiator.

Due to the wide temperature and pressure ranges, pneumatic valves of SITEC have been applied to control the flow, using a valve island, which used 6 bars compressed air to control the connected valves. A further advantage of using pneumatic valves was the possibility to integrate them into the safety concept as NO/NC valves (normally open valves/ normally closed valves) (see below).

To obtain the desired gas-flows with different gas compositions, thermal mass flow controllers F-230-AGD-11-V from Bronkhorst HIGH-TECH B.V. (I-1, I-2 & I-3 in Fig. 2) have been used for each pure gas. These controllers were capable to realize flows of 0.5 to 50 mL/min with a high accuracy for pure gases. The small dimensions of such a tubing system included the problem to find measurement techniques, which are able to work reliably in this environment. Sheath thermocouples (Type K, outer diameter 0.5 mm, length 200 mm, tube made of INCONEL) have been used to measure the temperature at important points in the facility (see measuring points I-11, I-12, I-15, I-16, I-21 in Fig. 2). Pressure detectors (in Fig. 2) were included for control purposes (I-19; P-522C-M40A-AGD-11-V from Bronkhorst HIGH-TECH B.V.) and for facility monitoring (I-6, I-8, I-38, I-22 (all of type P-3326 Wagner GmbH), I-17 (Type same as I-19)).

All starting products, in this case liquid isobutane, oxygen and initiator were conducted via an injection unit (Figure 3) into the micro reactor which was immersed as a spiral in a tempering bath of silicon oil (AK-10, Wacker Chemie Ag). Due to the

stability of the heat transfer medium and the steel tubing (Metal tube MC 200 S, LAUDA DR. R. WOBSEER GMBH & CO. KG, range: -60..350 °C) connecting the thermostat (H-2) and the tempering bath, the temperature of the tempering bath can be set to a maximum of 155 °C.

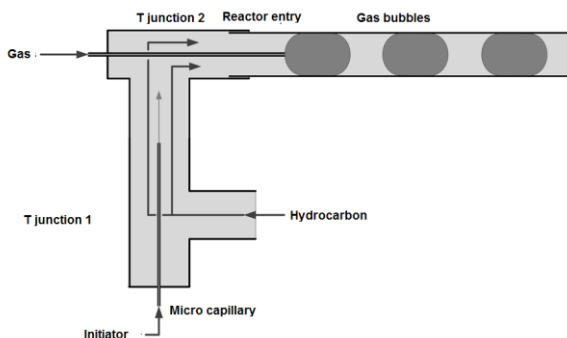


Figure 3. Injection unit with initiator, hydrocarbon and oxygen inlet and the entry of the reactor.

The most important challenge was the control of the reactor pressure. A pressure control by reducing the flow rate within a gas-liquid Taylor flow directly at the reactor outlet would lead to considerable pressure surges and flow pulsations. The problem has been resolved by separating the liquid phase from the gas phase and controlling the reactor pressure by releasing gas behind the waste vessel (B-4). The pressure control was realized by the pressure sensor I-19 (in Fig. 2) coupled in split range with two control valves (V-30) having different flow coefficients. This configuration allowed a wide range of gas-flows at different constant pressures. The mass flow was measured by a Coriolis mass flow meter M12P-AGD-11-O-S from Bronkhorst HIGH-TECH B.V. (I-20), measuring mass flow and density to quantify the gas flow so as to obtain the sample size of the gaseous phase.

A compilation of the selected design parameters is given in Table 2.

Table 2. Design parameters of the modular micro reactor facility for the oxidation of isobutane.

Parameter	Range ¹
Reactor pressure	1 - 100 bar
Reaction temperature	20 - 165 °C
Residence time	0.1 - 24 h
Reactor capillary inner diameter (ID)	0.5 - 4 mm
Reactor capillary length	1 - 100 m
Flow O ₂ , N ₂ , He	0.5 – 50 mL _N /min
Flow isobutane	250 - 10,000 mg/h
Flow initiator	3.4 nL/min - 3.52 mL/min

¹ these are minimal and maximal values. Not all combinations are possible.

A further challenge was the analysis of two-phase samples. We first aimed at analyzing continuously the product of the reaction by GC-MS, but this would have required an inappropriately high effort for the product processing since the samples needed to be available at 1 bar and 25 °C for analysis. Liquefied isobutane cannot be used as a solvent for GC, and continuous on-line analysis of such liquid gas samples was not feasible.

Due to the two phase character of the flow, a representative sample cannot be taken locally, but must include representative parts of the liquid phase as well as the gaseous phase collected over a certain time. As the length of the gas bubbles may

exhibit irregularities and the flow was often submitted to some pulsation, the collection time of the sample needed to be long enough to outbalance these differences.

The collection time for the liquid sample further depends on the quantity of the components – influenced by the conversion of the isobutane, the yield and the selectivity concerning the corresponding product - and its degree of dilution by some solvent, because the LOQ (limit of quantification) of the main products (or the LOD (limit of detection) for by-products) of the GC-MS needed to be taken into account.

Normally, the composition of a defined mass of a mixture of all reaction products has to be analyzed. This was not possible in the case of a multiphase reaction mixture. A separation of the phases was necessary since the phases could only be analyzed separately.

The liquid sample of the reaction mixture has been collected in container B-3 by opening V-24 for a defined period of time. After separating the container from the rest of the system by the valve V-24, the volatile sample components (isobutane, isobutene) are vaporized by pressure reduction. The corresponding gas/vapor flow was controlled by a mass flow controller M12+F-033CI-AGD-11-K-S from Bronkhorst HIGH-TECH B.V. (I-24), measuring simultaneously the density of the gas flow and the mass. The mass flow has been optimized to minimize losses of liquid reaction products during pressure reduction. The gas formed by pressure reduction of the liquid sample could be collected by a Tedlar bag (B-6) to enable a representative analysis of its content by GC-MS, because the composition of the gas during the vaporization would change if the gas was constituted by several gaseous compounds of different boiling points.

The oxygenated components, which were liquid at ambient conditions e.g. TBHP, DTBP, t-butanol (TBA), acetone, methanol, formic acid etc. (Shah et al., 2000) had to be absorbed completely by the solvent, present in the container for sample

collection to get a representative sample of a defined volume. Furthermore, the reaction needed to be quenched by a stop solution to “freeze” the state of the reaction mixture in the micro reactor and prevent any further reaction. Apart from DTBP, all polar oxygenated components were well soluble in water. Therefore, at first water had been tried as stop solution since it prevented further reactions better than other solvents. However, since DTBP has been used as initiator, it was still present in the reaction mixture so that the use of water was not possible. After verifying that there were no reactions taking place in the sample between the polar reaction products (e.g. ester formation by formic acid, condensation reactions) by comparing the results obtained with water and heptane, respectively, as stop solutions, heptane has been used to quench the reaction mixture.

Furthermore, a gas sample has been taken using a Tedlar bag from the content of the gas sampling pipe (B-5) and analyzed by GC-MS to obtain the composition of the gas phase.

3.4 Safety aspects and special construction aspects of the micro reactor

An important challenge of the micro reactor construction was the chemical instability of the hydroperoxides and peroxides used as initiators and present as intermediates and reaction products. Extensive thermal investigations showed that uncoated stainless steel or noble metals (especially copper, silver, gold) as well as many other materials (e.g. rubber, Viton, silicone) could not be used as part of the reactor components. Silicon and silicon carbide were the only inert materials (Willms, Kryk, Oertel, Lu, & Hampel, 2016). Therefore, the metallic parts being in contact with reaction medium or the initiator solution are made of stainless steel coated with amorphous silicon (Silcolloy[®] 1000 coating by SilcoTek[®]) by chemical vapor deposition (CVD) to prevent any reaction at higher temperatures and a falsification of the

experimental results thereby. Due to the oxidizing properties of oxygen, all fittings needed to be free from oil and grease. They have been specially cleaned by the respective manufacturer for use with oxygen. Furthermore, an oxygen compatible lubricant (GLEITMO 599) was used to lubricate the corresponding threaded connections of the bursting discs.

Before each experiment, a pressure test at the desired pressure using nitrogen has been performed for a minimum of 3 hours to verify that the leakage rate is below $1\text{E-}5 \text{ mBar}\cdot\text{l/s}$. For the further preparation of the reactor, nitrogen served to purge it in order to free the reactor from explosive mixtures. Furthermore, the pumps include additional valves to empty them. In order to clean the reactor walls, rinsing has been effectuated with the hydrocarbon.

To prevent any explosive atmosphere around the lab facility, it is placed in a large hood with a high air flow of $1200 \text{ m}^3/\text{h}$ comprising a hydrocarbon detector. All gas bottles have been placed in a ventilated fire resistant gas bottle cabinet (fire resistance 90 minutes).

Another very important part of the safety concept was the small inner diameter of 1 mm of the feed lines and the reactor tubing. By the high surface - volume ratio, an effective heat transport from the reaction mixture inside the reactor to the surrounding coolant was ensured. In the case of such a small diameter, a wall thickness of 0.3 mm was sufficient to ensure a pressure resistance of up to 300 bars. High pressure stability was also important in case that e.g. the gas bottle pressure-reducing valves - directly at the bottles - fail. To prevent any dangerous pressure rise, burst disks (response pressure 170 bar) were used, where the substances are safely drawn off into a blow-off tank in case of a pressure relief.

In all parts of the installation, a backflow of the fluid due to a pressure drop has been prevented by check valves (RV-1 to RV-11). A spontaneous release of the isobutane and oxygen gas bottles has been prevented by magnetic valves (V-42, V-43).

To prevent decomposition of the initiator inside the high-pressure syringe pump, the body of the syringe has been equipped with a cooling jacket and cooled down to approx. 10 °C by a coolant connected to a thermostat (H-1).

In case of an electricity failure or a loss of control air, there is no possibility to maintain a certain valve state. Therefore, the feed valves upstream the reactor have been designed as normally closed valves (NC), so any further delivery of substances is stopped. In contrast to this, the product valves downstream the reactor have been designed as normally open valves (NO) for the parts of the facility, where the reaction mixture and the pressure should be blown off. In case of an increase of temperature and/or pressure to a specified value, special NO valves will open, to draw off the whole reaction medium into the blow-off tank (B-2). The ventilation of the hood was monitored also (I.26). If ventilation failed (I-26), the facility did not blow off gases but only shut down thermostats, pumps as well as the gas feed to prevent the accumulation of an explosive gas mixture in the hood. For security reasons, also gas sensors (I-27) have been installed for the detection of high gas concentrations around the lab facility.

The LabVIEW software continuously verified if the measured pressure and temperature values exceed certain limits. The static limits define the experimental parameters of the lab facility which must not be exceeded to prevent any damage of the system. The variable limits guaranteed that the experimental conditions given by the operator are maintained during the whole course of the experiment. In case of a violation of these limits, the system is emptied by activating the corresponding FPGA software.

4 Functionality test of the lab facility

Preliminary to the reactive experiments, it was necessary to get an impression of the flow pattern in the capillary as a function of the molar ratio of isobutane and oxygen, in order to optimize the injection unit, to ensure maximum and reproducible liquid-gas phase boundaries as well as to evaluate the risk of a dry-out, which would reduce the effective phase boundary for the reaction. Therefore, preliminary investigations with the lab facility have been performed to study the Taylor-flow characteristics of nitrogen and isobutane in a glass capillary at various pressures ranging from 15 to 100 bars. Photographs from the flow have been taken and evaluated by an in-house software, which enabled the recognition of gas bubbles in the Taylor-flow in order to evaluate approximate values of the specific liquid-gas interface area, mean values of the gas bubble lengths etc. An example is given in Figure 4. The influence of the hollow gas injection needle on the Taylor-flow characteristics have been studied to assure an equal gas-liquid interface for all isobutane oxidation experiments.



Figure 4. Taylor flow of isobutane – nitrogen with 2.157 ml/min nitrogen (1.783E-03 m/s) and 826 mg/h Isobutane (5.284E-04 m/s) at a pressure of 35 bar and 25 °C.

The facility has been also used to perform oxidation experiments with isobutane and pure oxygen or oxygen - nitrogen mixtures, where isobutane is oxidized in a two phase process to TBHP, using DTBP as initiator. For this purpose, the pressure, the temperature, and the flow rates of isobutane, the initiator and oxygen have been set to preliminarily calculated values. A residence time of 4 hours was sufficient to realize a measureable conversion of isobutane. Heptane has been placed into the sample container B-3 as stop solution. After vaporization of the non-converted isobutane in the

container B-3, the reaction products have been analyzed by GC/MS. Figure 5 shows a chromatogram – split in two halves - of the resulting reaction mixture.

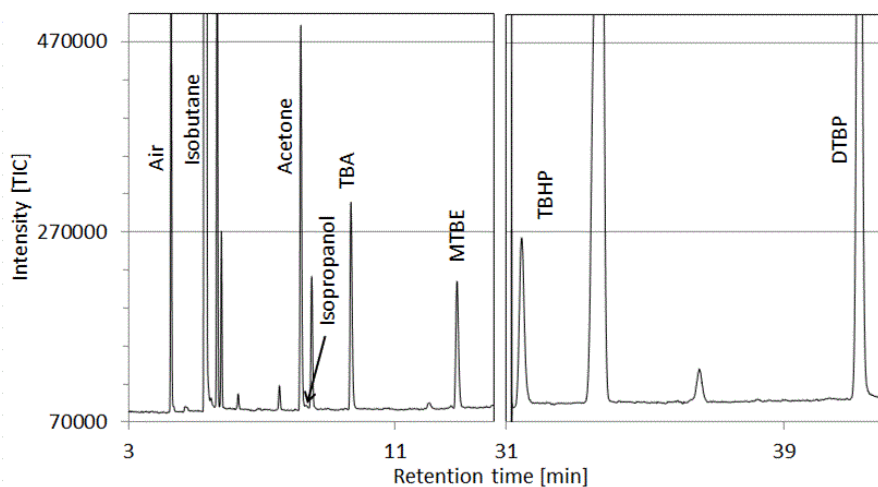


Figure 5. Chromatogram of the reaction mixture of the isobutane oxidation with 777 mg/ h isobutane, 18.42 μ L/ h DTBP and 10.12 mLN/ min oxygen at 50 bar and 130 °C. The unassigned peaks are due to impurities of the solvent heptane and the starting product isobutane.

Beside TBHP as the main reaction product, small quantities of TBA and acetone have been found originating from the decomposition of TBHP and/or the initiator DTBP. Methyl t-butyl ether (MTBE) has been used as internal standard. The peak of isobutane is due to the solubility of isobutane in heptane. Furthermore, we first identified isopropanol as a component of the reaction mixture. Further details on the GC/MS system, the GC method, sampling and reaction products are published elsewhere (Willms, Kryk, & Hampel, 2016).

Thus, the applicability of the experimental set-up for investigations of partial oxidations of hydrocarbons as two-phase flow processes in Taylor flow regime has been proven on the example of the oxidation of isobutane to form TBHP (Willms, Kryk, Wiezorek, & Hampel, 2014).

5 Summary and conclusions

The construction of a modular micro reactor for two-phase reactions appropriated to investigate a wide range of temperatures, pressures as well as liquid and gas flow rates for the realization of oxidation processes of hydrocarbons brought about several challenges. The required equipment, e.g. valves, measurement technics, pumps, for such a facility with a small tubing diameter was difficult to obtain and the realizable experimental parameters were often at the limit of the devices. Especially, high pressures were rarely acceptable for the commercial pumps. In the case of liquefied gases, these problems were still more important than in the case of normal liquids due to their exceptionally low viscosity, surface tension and density. Furthermore, a reliable and robust safety concept was required to ensure a safe long-term operation of the experimental facility since experiments often needed several days. Despite such challenges the design and construction of a modular micro reactor for the partial oxidation of hydrocarbons could be successfully achieved.

It is planned to investigate the influence of different initiators, reactor diameters and wall coatings. In the long term it might be preferable to replace the steel capillary by a silicon carbide micro reactor, which would enhance the safety of the experimental set-up, because the stability of the silicon coating is not guaranteed for a long time. Furthermore, it is planned to install an optical cell, which will allow to observe the Taylor flow as well as to distinguish a two phase flow from a supercritical mixture.

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