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Effect of Heterogenic Surfaces on Contact Angle Hysteresis: Dynamic Contact Angle Analysis in Material Sciences

By *Frank Rupp*, *Lutz Scheideler*, and *Jürgen Geis-Gerstorfer*[*]

1 Problem

Considerable economic damage is caused by biofilms on material surfaces originating when materials are in contact with aqueous biological systems. The fields concerned and the impacts are manifold. They cover material damage due to biofouling processes, bacterial loads of water lines (e.g. in hospitals, food processing industry) as well as inflammable processes caused by biofilms on biomaterial surfaces, e.g. on implants. Therefore, (macro)molecular interfacial reactions at the interface between material surfaces and the biological system are of basic interest for the development of advanced materials. One important aspect is the improvement of the long-term stability of implants. Interfacial reactions change relevant physical and chemical surface parameters, such as the surface free energy or the wettability. Questions arise on how these initial reactions influence the following biological answer of biofilm formation.

In the biomedical area, due to the contact of a biomaterial with the biological system, e.g. saliva, the initial surface state of a biomaterial is changed by hydration, by ion interfacial reactions and by protein adsorption. Due to bacterial adhesion a biofilm develops in the following steps. Thus, bacteria interact with a material's surface, which has been drastically changed by macromolecular adsorption. The initial, protein-rich film influences the following steps of bacterial adhesion and is therefore regarded to play a key role in biofilm formation processes. Basic studies of the initial, material-dependent formation of such layers are very important for the development of advanced surface modifications, which aim for example at surfaces, which reduce biofilms.

Recently, we successfully applied the classic Wilhelmy balance method and the dynamic contact angle analysis (DCA) on initial interfacial reactions of surface-modified biomaterials [1]. In this study, we present further results which underline the potential of these methods to yield time-resolved data of ionic and protein interfacial reactions. In contrast to many spectroscopic methods, an on-line method, which works time-resolved and without disturbing the interface, would be important in the process-engineered quality control. This is underlined by the fact, that many biomedical material surfaces currently are pre-biofunctionalized before their application in order to increase their biocompatibility and biofunctionality. The above-outlined statement of the problems involves many disciplines. In this approach, it is highlighted and discussed on the background of current research on biomaterials.

2 Wettability Analysis

2.1 Principles of Wettability Measurements and Contact Angle Hysteresis

The wettability of a solid surface is described with the contact angle. That is the angle between the base line of a liquid droplet, placed on a solid surface, and the tangent at the three-phase boundary solid/liquid/gas. At thermodynamic equilibrium, the contact angle is dependent on the surface tensions γ involved in the drop shape, which is described by the fundamental Young equation (Fig. 1a, Eq.(1)) [2,3]. The product of the surface tension of the liquid γ_{lg} and of the cosine of the contact angle $\cos\theta$ is termed wetting tension γ_{B}. Contact angles < 90 ° have a positive sign of the wetting tensions. That means, surfaces will be wetted by water and are hydrophilic. A complete wetting of solid surfaces is the result of very small contact angles, when the liquid spreads over the surface. The smaller the wetting tension becomes, the more unwettable the surface will be. In cases of contact angles > 90 °, the wetting tension has a negative sign.

$$\gamma_B = \gamma_{\mathrm{lg}} \cdot \cos\theta = \gamma_{\mathrm{sg}} - \gamma_{\mathrm{s}l} \tag{1}$$

Surface and interface tensions are dimensioned as follows:

$$\left[\frac{\text{work}}{\text{area}}\right] = \frac{\mathrm{Nm}}{\mathrm{m}^2} = \frac{\mathrm{N}}{\mathrm{m}} = \left[\frac{\text{force}}{\text{length}}\right] \tag{2}$$

Therefore, contact angles are experimentally accessible via force measurements if the surface tension of the liquid phase and the wetted length L (perimeter of the probe) is known.

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$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} = \frac{F}{L \cdot \gamma_{lg}} \qquad (3)$$

A method that is directly related to force measurements is the Wilhelmy method: probes, in most cases rectangular plates or also rods, are suspended from the beam of an electrobalance and immersed and emersed in liquid by raising and lowering a vessel, which contains the liquid (Fig. 1b). From the recorded force-length diagrams the buoyancy forces can be eliminated by linear regression to the immersion depth zero, separately for the immersion and emersion run. As a result, the obtained wetting tensions F/L are used to calculate the contact angles according to Eq. (3). The immersion run yields the advancing contact angle θ_{adv}, the emersion run the receding contact angle θ_{rec}. The difference between both angles is named the contact angle hysteresis H:

$$H \equiv \theta_{adv} - \theta_{rec} \qquad (4)$$

The existence of contact angle hysteresis is typically more the rule than the exception. Hysteresis is caused by variations between the real surface, which has to be measured, and an ideal, structurally and physicochemically homogeneous surface [4] (Tab. 1).

Effects of roughness on contact angle and on contact angle hysteresis have been published recently [5–8]. On the one hand, the occurrence of two distinguishable contact angles raises the question for the thermodynamically stable contact angle. Only this equilibrium angle would be in agreement with Young's equation. On the other hand, the contact angle hysteresis yields manifold information about the surface state of a material. If repeated immersion and emersion of a probe, i.e., multiloop Wilhelmy measurements, result in a constant hysteresis of the wetting tension and the corresponding calculated contact angles, the observed hysteresis is constant in the time course and therefore thermodynamically caused. In contrast to the thermodynamic hysteresis, kinetic hysteresis is there, if loop-dependent and therefore time-dependent changes in the hystersis are detectable. The reasons for kinetic hysteresis are manifold [4] (see Tab. 1). Phenomena, such as the swelling of polymeric surfaces [9] or the deformation of elastomeric material surfaces [10], are considered being involved in this type of hysteresis. Of great importance for this paper are kinetic hystereses (Fig. 1d) due to macromolecular adsorption out of liquids on solid surfaces. The hystereses have been qualitatively and quantitatively investigated by means of the dynamic contact angle analysis (DCA) on the basis of the Wilhelmy method. We applied the tensiometer Sigma 70 (KSV Instruments, LTD., Finland), a computer-controlled and fully automatic electrobalance equipped with a vertically movable probe desk for raising and lowering the liquid vessel.

Table 1. Causes for the hysteresis of wetting tensions and contact angles.

Thermodynamic hysteresis	Kinetic hysteresis
Roughness	Adsorption from the liquid phase
Reorientation of polymeric surface groups	Swelling
Chemical inhomogeneities	Deformation

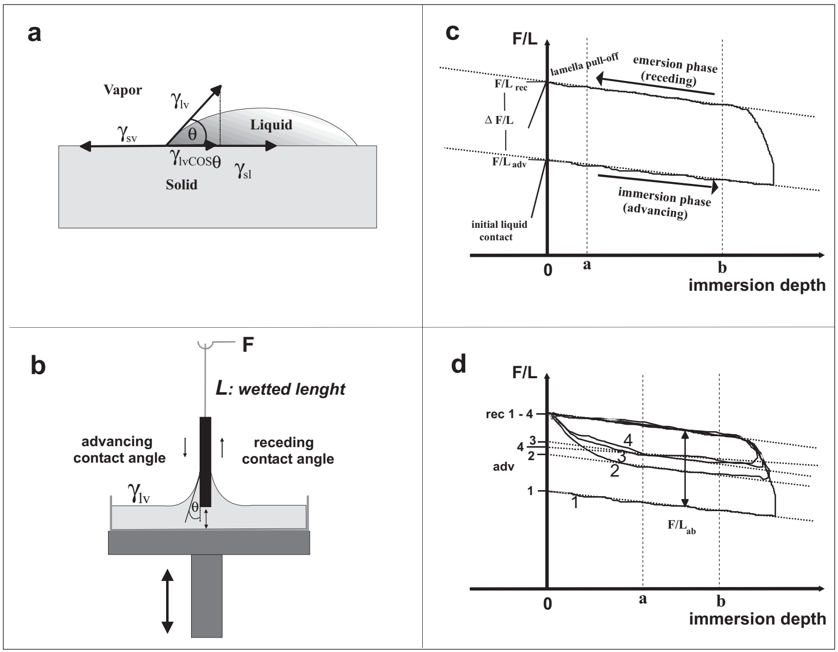

Figure 1. a – Graphic illustration of the Young equation (Eq. (1)) at the three-phase boundary of a sessile drop on a solid surface, b – Wilhelmy method, c – Single hysteresis loop of a Wilhelmy experiment with the wetting tensions F/L calculated in the interval a-b, d – Force-length plot of a four-loop Wilhelmy experiment: shifts of the immersion branches of the loops, which indicate kinetic hysteresis, can be described by the dynamics of the mean wetting tension F/L in the interval a-b.

Compared to the surface state before adsorption, the initial surface homogeneity or given heterogeneity of a solid surface is changed at the interface to a liquid phase if adsorption occurs. Therefore, kinetic hysteresis is a consequence of adsorption. Already in the early sixties, correlations between surface inhomogeneities and thermodynamic contact angle hysteresis had been investigated by Johnson & Dettre [11,12]. They found that surface chemical inhomogeneity is correlated with inhomogeneities of the surface energy which influences advancing and receding contact angles in a different way. In cases of surfaces with large high-energetic (hydrophilic) but small low-energetic (hydrophobic) areas, a liquid (water) is prevented from an undisturbed advancing by the hydrophobic patches. Thus, the advancing contact angle is larger than expected for the pure high-energetic surface. If the liquid recedes, hydrophilic surface patches delay the unwetting process due to a pinning effect. Hysteresis is directly due to the distinct sensitivity of wetting and unwetting processes on chemically heterogeneous surfaces. Hydrophobic surface areas of a heterogeneous surface influence much more the advancing contact angle than hydrophilic will do the receding (Fig. 2). According to Johnson & Dettre, the advancing contact angle is influenced from about 10 % hydrophobic, the receding contact angle from about 10 % hydrophilic surface patches on a hydrophobic matrix. On the basis of this empirically derived modeling, the difference of both species of contact angles can be interpreted as a function of the dispersion of chemical inhomogeneities. Due to interactions between solid surfaces with biological liquids, adsorption phenomena occur at the solid/liquid interface with the impact of time-dependent changes of the surface heterogeneity. The investigation of adsorption-caused shifts in advancing and receding contact angles and wetting tensions is the object of this contribution.

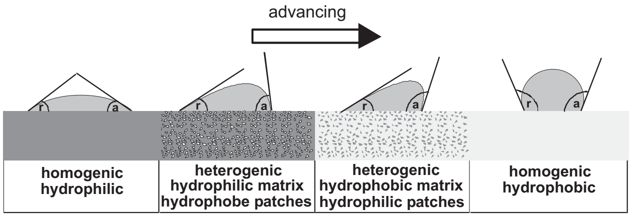

Figure 2. Contact angle hysteresis due to a different sensitivity of wetting and unwetting processes on heterogeneous surfaces; *a* advancing contact angle, *r* receding contact angle.

2.2 Dynamic Contact Angle Analysis (DCA)

The Wilhelmy method is dynamic, *primarily* because the solid and liquid phase moves relative to each other. As mentioned above, the dynamics in the advancing and receding wetting tension can be detected by means of the force loops. From these raw data, the advancing and receding contact angles can be calculated. Already one single Wilhelmy loop yields data for the calculation of the hysteresis of the wetting tensions and of the contact angles. *Secondly*, the dynamics of the Wilhelmy method is based on the occurrence of kinetic hysteresis effects visualized by multiloop measurements: the time dependency can be analyzed by the qualitative and/or quantitative evaluation of dynamic shifts in the immersion and emersion parts of the force-length diagram, respectively. If contact angles have to be calculated or if hysteresis shifts have to be visualized on the basis of shifts of the advancing and receding contact angles, a linear regression in the linear parts of the force diagram must be done (see Chapter 2.1). Due to nonequilibrium states during adsorption, in many cases the linear regression is not useful because there is no linearity in the force course. In such cases, the shifts can be analyzed by a loopwise calculation of the mean wetting tensions F/L in a fixed interval of the immersion depth [1]. The mean F/L can then be depicted as a function of the loop number. By this approach, the often descriptive analysis of hysteresis shifts can be complemented by quantitative data. If one is interested in desorption studies in addition to pure equilibrium adsorption measurements, multiloop experiments have to be made in series. For that purpose, multiloop desorption experiments are made in protein-free solutions directly after the adsorption multiloop run. The adsorption/desorption studies clarify the reversibility of the wettability status, which may have been changed during adsorption.

3 Results and Discussion

The possibilities and limitations of DCA are highlighted with several examples. It is a matter of experimental results from DCA studies with differently modified titanium plates. The experiments aimed at the material dependencies of the kinetics and equilibrium status of wettability changes during ionic and protein interactions on surface-modified titanium. These studies are embedded in the research field concerning biofilm (dental plaque) reduction on materials, which are in the oral cavity in contact with saliva.

3.1 DCA with Titanium Substrates

An essential finding is the very great variety in the wettability of titanium surfaces. Dependent on preliminary treatments, such as plasma cleaning, smoothing and polishing or wet chemical etching processes, the topography and chemical structure of the titanium surface is modified. The physical and chemical modifications may intensively modify the interfacial behavior of titanium in contact with aqueous biological systems. Cleaning procedures, such as the plasma cleaning, are known to etch the titanium surface and not only to remove surface contaminants. Pure titanium substrates, which were ultrasonically cleaned in ethanol and acetone, are typically characterized by a large thermodynamic wetting tension (contact angle) hysteresis due to very small, hydrophilic receding but much greater advancing contact angles. Kinetic hysteresis occurs as difference between the first and all following Wilhemy loops. They are due to the dry surface in the beginning of the experiment which is initially wetted during the first immersion loop. In contrast, air-plasma-cleaned titanium shows a very different wetting behavior. As with ultrasonically cleaned titanium, in multiloop experiments the receding contact angles are very constant, but the advancing angles show a very distinct dynamics. A very small hysteresis has been detected in the first loop (Fig. 3). But with the loop number the hysteresis increases and the titanium surface becomes successively hydrophobic. After ten loops the plasma-cleaned titanium shows the open hysteresis known from ultrasonically cleaned probes. The dynamics may have been caused by repassivation processes of the titanium oxide layer, which has been etched by the plasma treatment. In

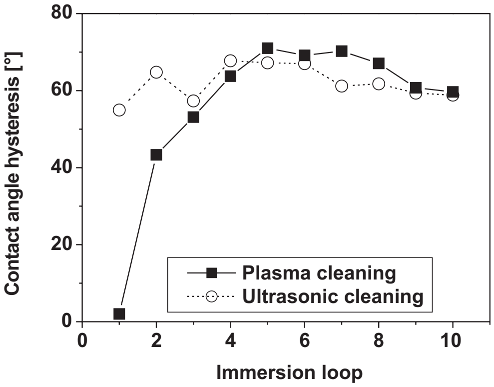

Figure 3. 10-loop Wilhelmy experiment with differently modified titanium in pure water (ethanol/acetone ultrasonically cleaned titanium and RFGD plasma-cleaned titanium).

addition, the hydrophilicity of the freshly cleaned titanium can be modified by hydration and formation of surface hydroxyl groups in water contact.

Similar phenomena of initially small contact angle hysteresis, successively increased by shifts of the advancing angle, can be observed with titanium substrates, which were chemically etched by Kroll solution [13]. The initial, very hydrophilic surface becomes hydrophobic during the experimental water contact.

Based upon these findings, in cases of titanium etchings done with the aim of an increased hydrophilicity we recommend to consider and investigate the long-term water and air stability of the initial hydrophilicity.

Titanium is chemically extremely reactive and passivates in a millisecond range by the formation of an oxide layer which leads to the well-known inert surface behavior. The native oxide layer is a few nanometer thick and resembles stoichiometrically titanium dioxide (TiO_2). In aqueous systems the TiO_2 surface becomes hydroxylated. Basic and acidic hydroxylic groups make the surface amphoteric with an isoelectric point (I.E.P.) of about pH 5 [14,15]. Therefore, the titanium surface has a positive net charge with pH < I.E.P., a negative net charge with pH > I.E.P. Though the titanium surface is characterized by extremely chemical inertness, its biological activity is very high. This activity is due to many surface modifying reactions which become possible in aqueous systems. In addition to pure hydration processes, in physiological solutions anion exchange reactions, able to change the chemistry of the surface and therefore to modify the wetting characteristic, are possible. An example for such an exchange are the interactions of phosphate anions, which have a high affinity for titanium [16]. $H_2PO_4^-$ and/or HPO_4^{2-} are publicized to exchange basic hydroxyl groups on the titanium surface [17]:

$$TiOH + H_2PO_4^- \leftrightarrow TiH_2PO_4 + OH^- \tag{5}$$

Dependent on the phosphate concentration, distinct kinetic hysteresis can be detected by multiloop Wilhelmy experiments. In this, the immersing branch of the loop is shifted to more positive wetting tensions and the hysteresis becomes smaller with increasing phosphate concentrations. This fact becomes obvious if the equilibrium data of the shifted wetting tension hysteresis is plotted against the phosphate concentration (Fig. 4). These findings are remarkable because proteins often are investigated in buffers containing phosphates. Kinetic hysteresis being found in such systems may pretend protein interactions, whereas the dynamic has mainly been caused by phosphate. Therefore, all components of a system, which is assigned to be analyzed by DCA, must be proven for their potential to cause shifts of the contact angle hysteresis.

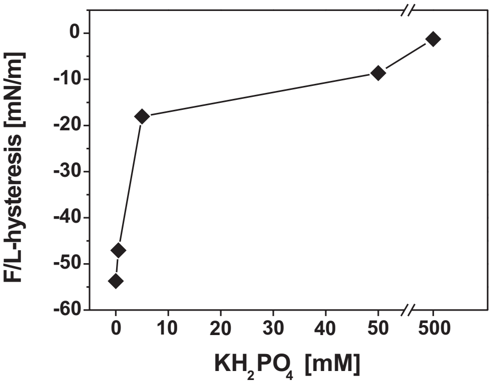

Figure 4. Interfacial reaction of phosphate anions and titanium (pH 7). The data show the equilibrium wetting tension hysteresis *F*/*L* of the tenth loops of multiloop Wilhelmy experiments.

3.2 Comparative DCA Study of Coated Titanium Substrates

Titanium plates have been coated by a dipping procedure with Teflon AF, an amorphous fluoropolymer, with TiAlN-TiN multilayer hard coatings by PVD (physical vapor deposition) and with quartz-resembling SiO_x coatings by a low-pressure plasma process. The water contact angles of these modifications are summarized in Tab. 2. Every one is characterized by thermodynamic hysteresis (see loop 1–10 in Fig. 5). The small contact angle hysteresis of both, of the hydrophobic fluoropolymer and of the SiO_x plasma coating, indicates very homogeneous surface modifications.

Table 2. Advancing (adv) and receding (rec) contact angles of the titanium modifications yielded from ten-loop Wilhelmy experiments in pure water. The equilibrium contact angles shown have been calculated from the tenth loop, respectively. The contact angle hysteresis is the simple difference between advancing and receding angles (adv-rec). Roughness parameters R_a have been determined by profilometry.

	Teflon AF	TiAlN-TiN	SiO_x
adv	125	72	53
rec	108	0	31
adv-rec	17	72	22
R_a [μm]	0.11	0.19	0.20

DCA results in characteristic kinetic hysteresis if BSA (bovine serum albumine) protein solutions were used as test liquids. The hysteresis shifts of titanium, TiAlN-TiN und SiO_x are primarily caused by shifts of the advancing wetting tensions. This indicates that each surface modification has increased its hydrophilicity due to protein adsorption. By that, the shifted and increased wetting tension leads to a stepwise reduction of the wetting tension hysteresis and indicates a homogenization of the surface (see loop 11–20 in Fig. 5).

In contrast, the fluoropolymer is characterized by a drastic fast shift of the receding wetting tension during the initial protein contact. This receding shift results in an initially distinctly increased hysteresis. Only in a second step a loopwise shifting of the advancing wetting tension and a decreased hysteresis, as with the other surface modifications, can be detected with the fluoropolymer/protein system. The protein interaction causes an initial heterogenization of the fluoropolymer surface and then a delayed successive homogenization. Already small protein concentrations are enough to strongly influence the receding contact angle. As described above, the sensitivity of the receding contact angle is owing to the pinning effect of smallest hydrophilic surface patches which are able to hinder and to delay the unwetting process. It was found out that the receding contact angle is shifted not below a threshold concentration of the protein of 5×10^{-4} g/l [1]. With smaller concentrations DCA could not detect any effects. Increased protein concentrations lead to a fluoropolymer surface with increased surface areas covered with hydrophilic protein surfaces. By that, the immersion branch of the force loop is affected to shift with a loopwise decreased hysteresis. By means of DCA the initial heterogenization of the fluoropolmer surface and the following homogenization, driven by further protein adsorption, can be detected. Whereas the pure water wettability status of the investigated material surfaces strongly differs, it is more assimilated by the protein interfacial reactions. In the twentieth loop of multiloop series experiments, i.e., the tenth loop of the adsorption run, the wetting tension hysteresis of all surfaces under research are strongly decreased (Fig. 5). Differences between the materials manifest themselves during the two desorption multiloop experiments in protein-free solution (loop 21–30 and 31–40), which were measured directly after the adsorption run (loop 11–20) and give information about the reversibility of the macromolecular interaction. According to our DCA results, the BSA interaction with the fluoropolymer surface is partially irreversible. The small hysteresis after the adsorption becomes very enlarged after desorption took place. This behavior is in contrast to the wettability changes of the other surfaces, which DCA characterizes as largely reversible.

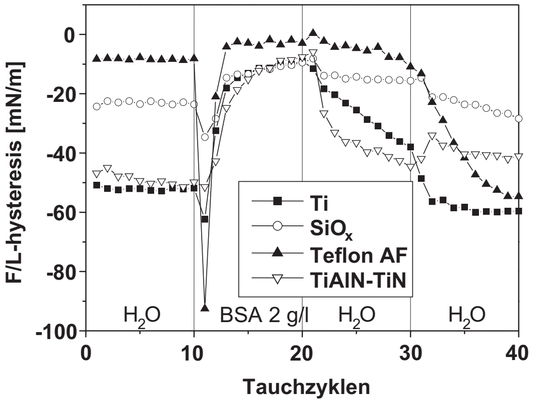

Figure 5. Adsorption-/desorption of BSA 2g/L H_2O (pH 7) on differently modified titanium by means of a series Wilhelmy experiment. Four single 10-loop experiments run directly one after the other: loop 1–10 in H_2O (base line), 11–20 in protein solution (adsorption), 21–30 and 31–40 in H_2O (1st and 2nd desorption). The diagram shows the mean wetting tension hysteresis ($\Delta F/L$) calculated in the 10–12 mm interval of the immersion depth with a maximum depth of 15 mm.

To summarize, the above-presented method, here applied to biomaterials research, is a useful tool to evaluate initial wettability characteristics of material surfaces. In our opinion, the DCA can be applied without problems to other research fields.

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Potential of Pollutant Treatment by Combined Extraction and Oxidation with Supercritical Carbon Dioxide*

By *Andrea Kruse***, *Nicolaus Dahmen* and *Eckhard Dinjus*

Compressed gases in the liquid or supercritical state can be used as solvents and reactants. This possibility can be exploited in the dense gas extraction of pollutants from solids or liquids. The pollutants removed in this way can then be decomposed completely by total oxidation after air has been added. The possibilities and the potential of the combined process are discussed on the basis of laboratory-scale studies of both extraction and oxidation on model substances.

1 Introduction

Carbon dioxide, CO_2, is the gas most frequently used for dense gas extraction because of the absence of any health hazards, its non-flammability, ease of technical handling, and high availability. The critical point of CO_2 is at 31 °C and 74 bar. Under pressure, and at temperatures not far above the critical temperature, CO_2 has densities similar to those of a liquid, and a considerable capability to dissolve many organic substances, which can be varied by means of the pressure and temperature. These characteristics can be used to separate substances at high density and remove them again, for instance, by changes in pressure or temperature. The extractant regenerated in this process can be recycled into the extraction process. After separation, the pollutants removed are present as solvent-free concentrates which must then be disposed of for good. In order to reduce risks in transit and further handling, CO_2 can be used first to extract pollutants from solid or liquid residues and then destroy the concentrate without any further intermediate treatment. For this purpose, the appropriate oxidation step is added to the extraction plant.

A procedure of this kind was discussed already by Michelfelder *et al.* [1], where extraction with supercritical CO_2 was employed as an upstream pretreatment stage of supercritical wet oxidation (SCWO). This technically more expensive process can be circumvented by having also the oxidation step proceed in supercritical CO_2. The experiments performed for this purpose show that the decomposition of organic substances proceeds as effectively as in supercritical water. Another option is the decomposition of organic matter by indirect electric oxidation, which can also be coupled with extraction [2].

2 Oxidation in Supercritical Carbon Dioxide

Fig. 1 shows the flow sheet of the experimental device in which the decomposition of model substances representing pollutants was studied by oxidation in CO_2 in an excess of airborne oxygen. CO_2 is premixed with the pollutants, and air is supplied at the reactor inlet. All three flows are first preheated. At temperatures of up to 550 °C and a pressure of 250 bar, the organic substances are converted into water and carbon dioxide by the oxygen in the continuously operated tubular reactor (6 m long, 2.1 mm I.D.) at residence times of up to 10 s and thus decomposed completely. Subsequently, the reaction mixture is cooled and expanded downstream of a backpressure controller. In this step, it separates into a liquid and a gaseous phase. Samples were taken of both phases, and the decomposition products were identified and quantified [3].

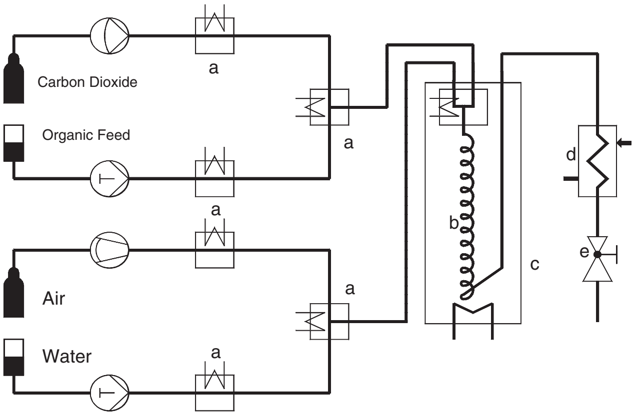

Figure 1. Schematic diagram of the test facility for oxidation in supercritical CO_2. a: preheater, b: tubular reactor, c: fluidized sand bed, d: chiller, e: backpressure controller.

The setup was used to study the oxidation of various model substances and their mixtures [4]. Particularly high conversion rates at short residence times were obtained whenever the mixture ignited. Ignition, in this case, refers to a local temperature increase with particularly high conversion rates. This is shown in an example in Fig. 2. For methanol and ethanol, conversions with respect to the carbon content in the educt ranged up to 99.9 %, and for toluene to more than 98 %.

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