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Glucose oxidation in a three-phase stirred airlift reactor: experiments and model

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Abstract

The three-phase catalytic oxidation of glucose into gluconic acid is studied in a new type of reactor: a stirred internal-loop airlift reactor. The influence of oxygen flow rate and of agitation on reaction rate are experimentally checked. By means of a model, a better knowledge of the reaction kinetic order for oxygen is reached. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Stirred airlift reactor; Three phase; Kinetics; Experiments; Model

1. Introduction

Catalytic gas–liquid–solid reactions form a wide but complicated theme of research. Such reactions need transfer of gas or liquid reactants towards the pores of particles; the proper catalytic phenomena take place in the pores, at the surface. These reactions also suppose transfer of the appeared chemical species in the opposite direction.

The kinetics of catalytic reactions are usually studied in mechanically stirred reactors. The present work deals with the oxidation of glucose into gluconic acid. This reaction has already been studied in stirred reactors, bubble columns or fixed beds [1,2]. We have carried it out in an internal loop airlift reactor equipped with an agitator (propeller): this new type of reactor has previously been investigated in terms of hydrodynamics and mass transfer with the air/glucose (aqueous solutions) systems.

A priori the use of an agitation system within an airlift reactor generates an additive cost. For some reactions however, the gaseous reactants are expensive, or toxic, and cannot be recycled. The gas feed has then to be as moderate as possible – it may correspond to stoichiometric conditions for the reaction. Then, if the airlift reactor is run with a three-phase medium, the low liquid circulation velocity generated by a moderate gas flow rate does not allow catalyst particles to be fluidised. Mechanical agitation provides in this case a precious help. Through the example developed in this work, one can see how a stirred airlift reactor allows satisfying operating conditions. On the other hand, gas recycle, when it is possible, is still much more expensive than mechanical agitation. That is why stirred airlift remains attractive for industrial applications.

What is more, it is very useful to reach low gas flow rates in a pilot scale stirred airlift reactor: under such operating conditions kinetic parameters are easily identified.

The purpose of this work is to determine the influence on the apparent kinetics of a reaction of various

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parameters, and particularly of gas flow rate, agitation speed and oxygen concentration. The chosen reaction, oxidation of glucose, is an example which does not need a weak gas flow rate, but it allows us to show the conditions of operation that give a maximum reaction rate for a minimum oxygen flow rate. A model is also proposed so that a better knowledge of oxygen influence on the kinetics can be reached.

2. Focus on oxidation of glucose

Literature gives some information on oxidation of glucose: it takes place in three-phase medium; the catalyst is constituted of solid particles of Pt. Previous studies [3] led to the identification of secondary products and to a good description of catalyst activity and poisoning. Nikov and Paev [1] realised a wider investigation of this reaction in a stirred tank and determined appropriate conditions of operation with 3.5% (w/v) of a palladium catalyst deposed on Al_2O_3. For this series of experiments, the liquid solution was saturated with oxygen: its concentration $[O_2]_L$ was 1 mmol/l; authors also identified the kinetics of reaction. They modelled reaction rate as follows:

$$r = \frac{d[GL]}{dt} = \frac{k[GL]m}{1 + K[GL] + K_p[AGL]}, \quad (1)$$

where [GL] and [AGL] are the concentration of glucose and gluconic acid in the liquid phase, respectively; k is the kinetic constant of reaction; K and K_p are the adsorption equilibrium constants of glucose and gluconic acid, respectively; and m is the mass of catalyst in the reactor per volume of liquid.

k, K and K_p have been identified by Nikov and Paev [1]:

$k = 0.0473\,\mathrm{l/g\,min}$,

$K = 0.0138\,\mathrm{l/mmol}$,

$K_p = 0.0279\,\mathrm{l/mmol}$.

3. Experimental set-up

The experimental set-up is shown in Fig. 1. The airlift reactor is constituted of two co-axial tubes; their diameters are 60 and 100 mm, respectively, and their heights are 1 and 1.5 m, respectively. A propeller

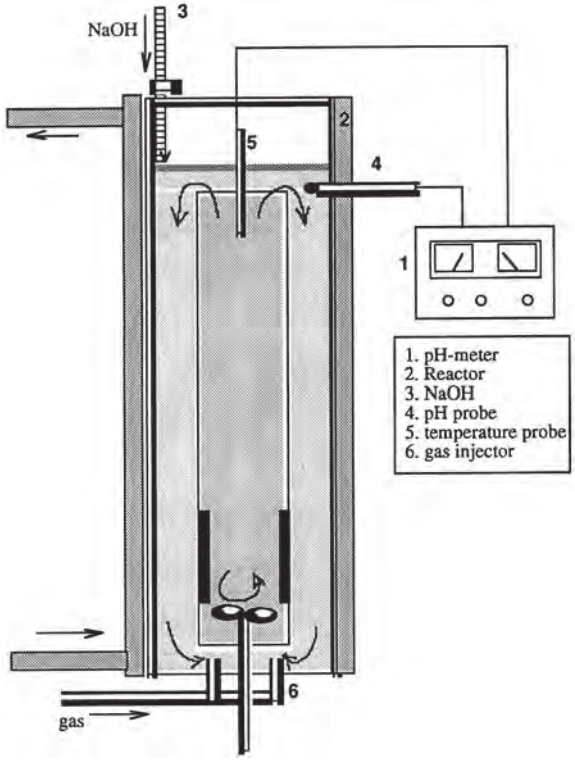

Fig. 1. Schematical set-up.

stands at the bottom of the central column. A circulation of warm fluid inside the wall of the central column maintains the whole medium at the desired temperature. Gas is fed at the bottom of the inner tube and creates a difference in density between the two columns. That is why liquid circulates upwards in the central tube (called 'riser') and downwards in the annular zone (called 'downcomer').

Precise operating conditions for this reactor have been chosen for oxidation of glucose:

- temperature, 50°C: values of k, K and K_p have been determined at this temperature [1];
- pH=9: this is allowed by successive addition of a 12 N solution of NaOH;
- $[GL]_0$=0.4 mol/l;
- catalyst: Pd on Al_2O_3, d_p=50 μm, ϵ_s=3.5% (w/v).

The characteristics of catalyst particles (d_p and ϵ_s) have been chosen in relation with the work of Nikov and Paev [1]: they have proved that inner diffusion inside the particles has no influence provided ϵ_s is

lower or equal to 3.5% (w/v) and if particle diameter is in the range [45–80 μm].

4. Experimental results

4.1. Influence of oxygen concentration

To identify the influence of oxygen concentration, which has not been studied by Nikov and Paev [1], various oxygen/nitrogen gaseous mixtures have been used. For four values of oxygen concentration in the gas phase, the quantity of added NaOH, which varies linearly with glucose consumption, is reported in Fig. 2. Fig. 3 shows the evolution of reaction rate versus time. The reaction rate strongly increases with the oxygen concentration in gas, and a total conversion seems to be reached within an hour, whereas only 50% conversion are performed within two hours when experiments are run with air.

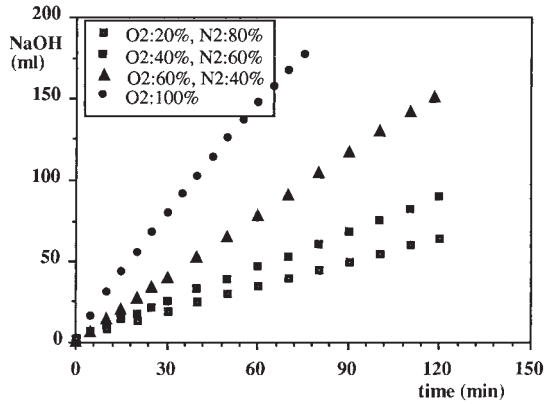

Fig. 2. Effect of oxygen concentration on glucose oxidation.

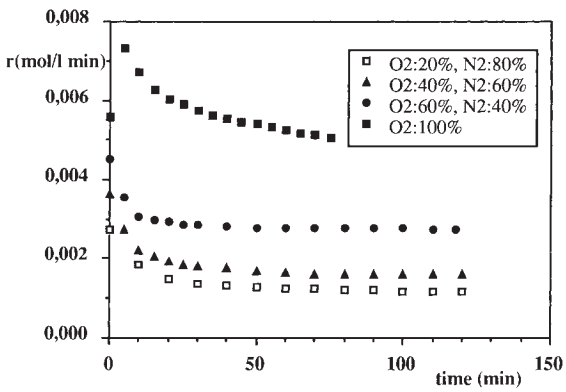

Fig. 3. Variation of reaction rate versus oxygen concentration.

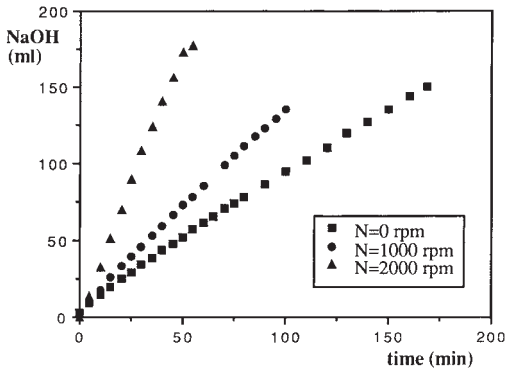

Fig. 4. Effect of rotation speed of stirrer on glucose oxidation.

4.2. Influence of agitator rotation speed

Experiments have been run under several conditions of agitation (rotation speed: N=0, 1000 or 2000 rpm); they put in evidence the important action of agitation (Fig. 4): the higher the N, the faster the reaction rate is.

4.3. Influence of gas flow rate

For N=2000 rpm and pure oxygen feed, the various values of gas flow rate that have been tested clearly show that the observed reaction rate does not depend on gas flow rate as soon as the superficial gas velocity U_g is higher than 1.17 cm/s (Fig. 5): the chemical regime is reached. For U_g<1.17 cm/s however, mass transfer is the slowest step.

Without any agitation (Fig. 6), the chemical regime is observed for stronger gas flow rates: U_g=2.35 cm/s.

The chemical regime is also reached with air as the gas phase (Fig. 7).

5. Modelisation

As said in Section 4.1 of this work, the effect of oxygen on glucose oxidation has been identified but not quantified. We use here the kinetic relation proposed by Nikov and Paev [1], assuming that

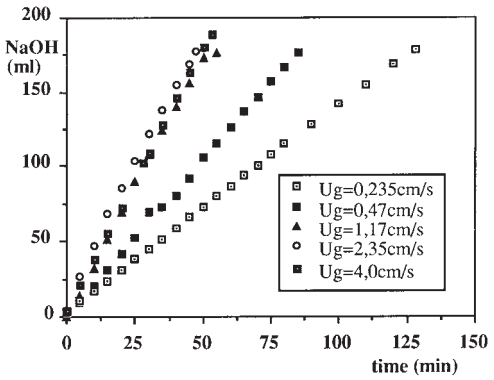

Fig. 5. Effect of gas velocity (oxygen) on glucose reaction N=2000 rpm.

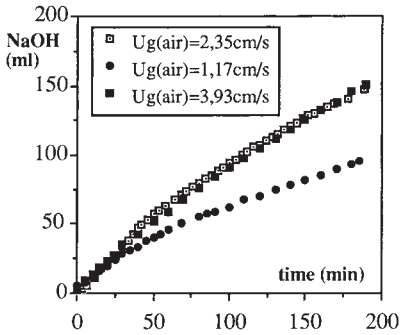

Fig. 6. Effect of gas velocity (air) on glucose oxidation N=2000 rpm.

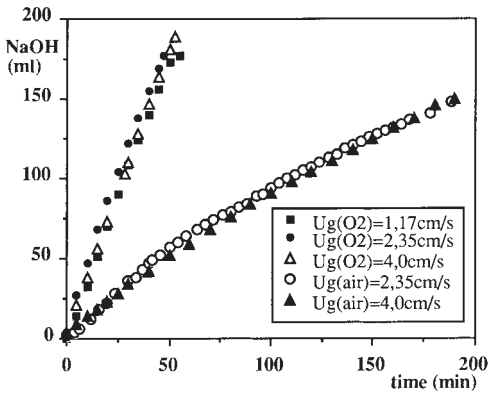

Fig. 7. Identification of chemical regime N=2000 rpm (oxygen in air).

the reaction shows an order 'α' in regard with the oxygen concentration in liquid phase. By fitting the model to the experimental results, we expect to determine α.

5.1. *Settling the model*

5.1.1. *Assumptions*

The kinetic law of Nikov and Paev has been derived using data collected in a stirred tank. To use this law, we must assume that our own reactional medium is perfectly mixed. Indeed, the hydrodynamical investigation of our internal-loop airlift reactor [4] has proved that the time needed to homogenise concentration of a tracer inside the reactor (t_m=100 s) is, thanks to liquid circulation, extremely short in regard with reaction and mass transfer time (around 100 min).

The system can then reasonably be considered isothermal: we checked that the temperature inside the reactor does not vary during an experiment.

We now assume that the whole reactional medium (solid, liquid and gas) is of constant volume: solid holdup is stable, and negligible anyway; gas retention may vary with the physico-chemical characteristics of the medium, because very fine bubbles may appear and circulate through the whole loop, increasing the global volumetric gas flow rate in the riser. But we measured the global gas holdup in the reactor during the experiments by means of the manometric technique, and no variation of volume was detected. Eventually, the liquid volume in the column depends on the numerous samplings and soda additions. But the maximal relative global volume variation that we observed never exceeded 1%.

We even consider that the liquid–solid mass transfer is not a limiting step; this means that the concentration of any chemical species present in the reactor has the same value in the liquid and in the solid phase. We also suppose that the oxygen solubility does not depend on concentration of glucose or gluconic acid, and then that it is stable under our operating conditions. Furthermore, oxygen concentration being weak in the liquid phase (less than 1 mmol/l), its adsorption at solid surface can be neglected.

Pointing out that our system is closed for liquid and solid phases, and open for the gas one, we can now give the equations of the dynamic model.

5.1.2. Equations

Using the kinetic law proposed by Nikov and Paev [1] and assuming an order α for oxygen concentration, we derive mass balance equations for oxygen, glucose and gluconic acid in the liquid phase:

$$\frac{\mathrm{d}[\mathrm{GL}]}{\mathrm{d}t} = \frac{k[\mathrm{GL}][\mathrm{O_2}]_\mathrm{L}^\alpha}{1 + K[\mathrm{GL}] + K_\mathrm{p}[\mathrm{AGL}]} \frac{M}{(1-\epsilon_\mathrm{g})V_\mathrm{r}} \tag{2}$$

where M is the total mass of catalyst, ϵ_g is the global gas holdup in the reactor, and V_r is the total volume of reacting medium.

$$\frac{\mathrm{d}[\mathrm{O_2}]_\mathrm{L}}{\mathrm{d}t} = -\frac{k[\mathrm{GL}][\mathrm{O_2}]_\mathrm{L}^\alpha}{1 + K[\mathrm{GL}] + K_\mathrm{p}[\mathrm{AGL}]} \frac{M}{(1-\epsilon_\mathrm{g})V_\mathrm{r}} + k_\mathrm{L}a([\mathrm{O_2}]_\mathrm{L}^* - [\mathrm{O_2}]_\mathrm{L}), \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{AGL}]}{\mathrm{dt}} = -\frac{\mathrm{d}[\mathrm{GL}]}{\mathrm{dt}}. \tag{4}$$

The initial conditions are:

- $[\mathrm{GL}]_0$=0.4 mol/l,
- $[\mathrm{AGL}]_0$=0 mol/l,
- $[\mathrm{O2}]_{\mathrm{L}0}$=0 mol/l (because the reactor is aerated with nitrogen till the experiment begins).

These equations have to be solved and the calculated values of the various concentrations are to be compared with experimental results. Mass transfer coefficient $k_\mathrm{L}a$, however, was not measurable during the experiments. This coefficient strongly depends on the interfacial area of the reacting system, but also on gas holdup, interfacial tension, temperature and local hydrodynamics around bubbles. For the [oxygen/glucose and gluconic acid] system, the value of $k_\mathrm{L}a$ is probably very far from its value in the non-reacting [oxygen/glucose] system (the latter has been measured in a previous work [4]).

Two parameters have then to be identified by the model: α and $k_\mathrm{L}a$.

5.2. Model solution

The ordinary differential Eqs. (2), (3) and (4) are solved through a fourth order Runge–Kutta–Merson method. Optimal values of α and $k_\mathrm{L}a$ are reached by use of an optimisation method: the difference between the calculated glucose concentration and the experimental one is minimised. This difference is 'the objective function' and named FOB. The FOB function is plotted versus α and $k_\mathrm{L}a$ in Fig. 8. It puts in evidence the optimal couple of solutions: α=0.59 and $k_\mathrm{L}a$=4.58 min^{-1}. Implementing the model with these values, we compare the calculated concentration of glucose versus time with its experimental evolution, as

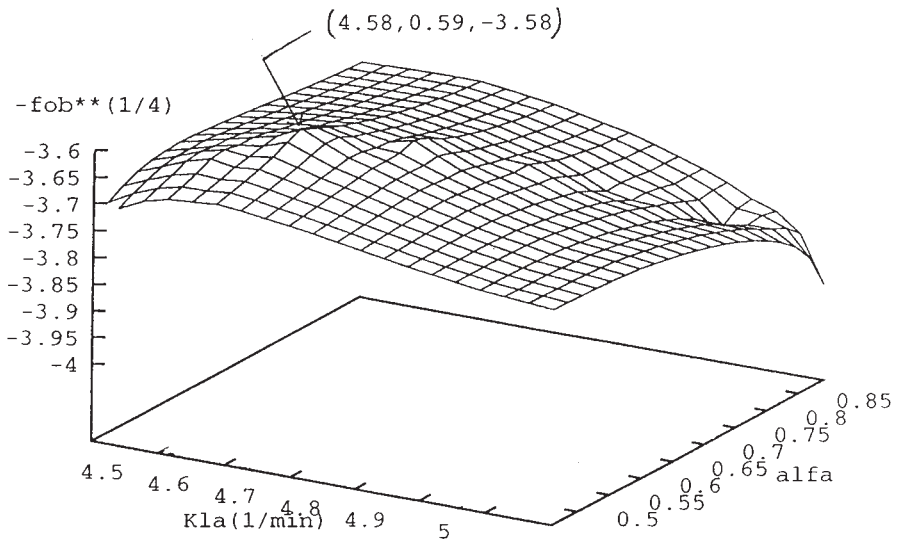

Fig. 8. Function FOB of model versus α and $k_\mathrm{L}a$.

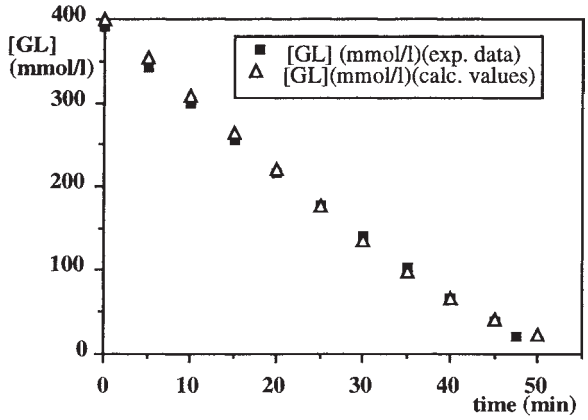

Fig. 9. Comparison between model values and experimental data.

shown in Fig. 9. This figure corresponds to the following experimental conditions:

- T=50°C,
- pH=9,
- U_g=2.35 cm/s,
- N=2000 rpm,
- ϵ_s=3.5% (w/v).

5.3. Comments on results

5.3.1. Order of reaction α for oxygen

It is clear that the reaction cannot be of zero order with oxygen: experiments showed that the amount of oxygen in the feed gas has a great influence on reaction rate (see Section 5.1.).

The order of magnitude of the calculated value of α seems to be correct. But it strongly depends on the identified value of k_La, as is shown in Fig. 8.

5.3.2. Mass transfer coefficient k_La

The identified value of k_La (4.6 min^{-1}) is much higher than the experimental value that was measured in the non-reacting system (2.6 min^{-1} [4]). This discrepancy may be justified by the electrolytic nature of the reacting system, which contains some soda. This medium probably inhibits bubble coalescence and increases the interfacial area and k_La, as a consequence. Indeed, the global gas holdup in the reactor has been measured during the experiments of oxidation; its value is about 20% higher than the gas holdup observed without reaction, for similar conditions of temperature, gas flow rate and solid retention. This proves that bubbles have a weaker mean size in the reacting system, offering a larger exchange area.

The order of magnitude of the identified k_La for the reacting system is then plausible.

5.4. Conclusion

This attempt to model the oxidation of glucose in an internal-loop airlift has put in evidence the actual participation of oxygen in the kinetics. But we only found an order of magnitude for the corresponding kinetic order: α is about 0.5. The model would be more precise if we could measure the exact value of k_La in the reacting sytem.

6. General conclusion

The purpose of this work was to realise the oxidation of glucose in a new type of reactor: a stirred internal-loop airlift reactor. Some results have been pointed out.

First, agitator rotation speed has a strong influence on reaction rate; indeed, using air as feed gas and choosing N=2000 rpm, we even get better performances than we can get with oxygen and under no agitation.

We have also characterised the oxygen contribution to the kinetics of glucose oxidation. However, the experimental value of k_La for the reacting system is needed to determine precisely the order of reaction towards oxygen.

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