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Catalysis Today 24 (1995) 165–171

CATALYSIS TODAY

Development of a continuous catalytic heterogeneous column reactor with simultaneous extraction of an intermediate product by an organic solvent circulating in countercurrent manner with the aqueous phase

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Abstract

A new solid–liquid–liquid reactor has been developed in order to simultaneously benefit from the advantages of both the catalytic activity and molecular sieve properties of the zeolites, the superior performances of concentration gradient reactors for positive order consecutive chemical reactions and the extraction of an intermediate target product by a solvent with countercurrent flows. The first reaction experimented with, was the acido-catalyzed dehydration of the hexoses into 5-hydroxymethylfurfural. The study was divided in two parts: (1) laboratory tests in a 0.3-liter batch reactor where mordenites were found to be the most selective catalysts, (2) chemical engineering studies: first, hydrodynamic tests where the systems tested ([water · hexose · zeolite]–methylisobutylketone) enable large through-put capacities, second, chemical tests in a stainless steel pulsed column of 25 mm in diameter and 8220 mm in height. Simultaneously, some simulations have been executed on a software designed by CEA for liquid–liquid extractions and modified by introducing chemical reactions.

1. Introduction

After the 1950's, solid catalysts radically changed the petrochemical and refinery industries with such varied applications that they required the design and implementation of new types of diphasic or triphasic reactors [1].

Of these different catalysts, there are the crystalline aluminosilicates, called zeolites, which are also used for their properties as ion exchangers, adsorbents and molecular sieves. Due to the possibility of simultaneously benefitting from several of their properties, the zeolites are increasingly tested in organic synthesis [2]; their excellent thermal stability and the relative ease of their recovery and their regeneration by simple calcination also contribute to the use of zeolites in the new processes which seek to protect the environment.

Within the scope of their respective activity in organic chemistry and chemical engineering, the URA CNRS 418 at ENSCM and the CEA have begun work in the acido-catalyzed dehydration of carbohydrates which can provide basic compounds for the synthesis of new furanic polymers of technical and economic interest [3]. In these reactions, until now catalyzed by mineral or

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0920-5861/95/$09.50
SSDI 0920-5861(95)00026-7

organic acids or resins [4], the target product — for example furfural or 5-hydroxymethylfurfural — is an intermediate component of consecutive reactions which are sensitive to the same operating parameters, which makes it difficult to control the reaction selectivity. To alleviate this drawback, processes have been developed [5,6] to selectively extract the intermediate component formed by a solvent so as to make it inert. However, the selectivities remained limited — less than 70% — due to:

- either the dilution of the acid throughout the reactive aqueous phase,
- or a batch operating mode and the single extraction stage.

Depending on these data, we have undertaken work towards the development of a continuous process combining, on the one hand, the acidity and molecular sieve properties of zeolites, and, on the other hand, the simultaneous extraction by a selective solvent of the intermediate target product [7]. Implementation of this process requires a triphasic solid–liquid–liquid (S–L–L) reactor. To our knowledge, no such reactor exists on an industrial scale. Indeed, all the triphasic reactors developed in the petrochemical industries, and more recently in fine chemical synthesis [8], contain, in addition to the solid catalyst (S), a gaseous phase (G), and a liquid phase (L), with each one of the fluids containing a reactive component. We have therefore conducted both the process research (ENSCM) and the technology research (CEA), with ongoing exchange. Hopefully, this approach will be seen in the following discussion of our work and results.

2. Process research: choice and use of zeolites

The first reaction experimented with was the acido-catalyzed dehydration of the hexoses into 5-hydroxymethylfurfural.

2.1. Experiment

2.1.1. Catalysts

After a literature search on the mechanism of the reaction under study, and data from the URA CNRS 418 experiment on acid solid catalysis, four aluminosilicates in protonic form were selected: H-Y-faujasite, H-mordenite, H-beta and H-ZSM5; their acid character is a function of the Si/Al ratio and can be easily adjusted through dealumination procedures. Given the concern with the development of the process, this selection was voluntarily oriented toward commercially available zeolites; the above-mentioned products were supplied by PQ Zeolites, Uetikon and Zeocat.

2.1.2. Reactor and operating conditions

The laboratory tests were carried out in a 0.3-liter stirred autoclave operating in the batch mode, heated by electrical resistances, equipped with 2 valves for sampling the aqueous phase and the organic phase after stirring stops.

The procedure was as follows: hexose or precursor (1 to 7 g), zeolite (0.5 to 2 g), water (35 ml) and methylisobutylketone (175 ml) — considered to be a good solvent for industrial use for HMF extraction — were poured into the reactor. After the reactor was closed, it was made inert by the introduction of nitrogen under 10 bars, the heating and stirring were put into action. When the temperature reached the process temperature, the first sample was taken and this instant is referred as zero time in the following.

2.1.3. Analyses

The liquid intake and output phases were analyzed by HPLC chromatography:

- aqueous phases: strong ion-exchange resin in H^+ form; detector: refractometer; mobile phase: trifluoroacetic acid 10^{-3} M;
- organic phase: PLRPS 5 column; detector: spectrophotometer 280 nm; mobile phase: methanol/water (70/30 by volume).

2.2. *Results and discussion*

The conversion performances (converted fructose/initial fructose) and the selectivity (mol HMF/ mol converted fructose) are summarized in Table 1.

They turn out to be simultaneously dependent on the zeolites' acidity and on their structural properties. The highest fructose conversions are obtained with the H-Y-faujasites for Si/Al ratios of 15, with the H-mordenites for Si/Al ratios of 11. The best selectivities (90%) are provided by the mordenites. This is probably due to the shape selective properties of the mordenites which are made up of large pores with a tubular bi-dimensional structure, and which, unlike the faujasites, do not possess large cavities enabling the formation of polymers.

The kinetic analysis shows that the dehydration of the fructose in HMF corresponds to consecutive reactions of order 1.

Differences are observed in the concentration ratio HMF in the organic phase/HMF in the aqueous phase, depending on the nature of the zeolite (0.8 with the mordenites, 1.2 with the faujasites). These differences can be attributed to shape selective properties but also to chemical phenomena (diffusion of the reaction products) or thermodynamic balances. We have undertaken a study to clarify this point, which, for certain applications, can influence the choice of the industrial catalyst and of the reactor type.

Table 1
Process research experiments: conversion of fructose and selectivity to 5-hydroxymethylfurfural after 30 and (60) minutes of reaction at 165°C

Catalyst	Si/Al	Fructose conversion (%)	HMF selectivity (%)
None		15 (32)	40 (38)
H-beta	15	75 (85)	44 (40)
H-ZSM5	25	82 (90)	56 (59)
HY-faujasite	2.6	47 (68)	38 (29)
HY-faujasite	10	60 (74)	70 (56)
HY-faujasite	15	57 (76)	54 (53)
HY-faujasite	20	23 (45)	75 (63)
H-mordenite	7.5	36 (57)	96 (77)
H-mordenite	11	54 (76)	92 (91)
H-mordenite	49	59 (62)	66 (70)
H-mordenite	100	31 (48)	72 (81)

Depending on these results, the chemical engineering studies will involve a continuous triphasic reactor–extractor:

- with a concentration gradient which provides conversion and selectivity performances superior to those obtainable from a stirred slurry reactor in the case of positive order consecutive reactions;
- with countercurrent flows of the two fluid phases.

3. Chemical engineering studies

3.1. *Reactor–extractor with fixed-bed zeolites*

The first idea was to deposit the extruded zeolites in a fixed-bed column reactor, where the two liquid phases (reactive sugared aqueous phase and HMF extracting solvent) moved gravitationally in a countercurrent direction across the bed. In order to simultaneously increase the kinetics of the chemical reaction and of the liquid–liquid transfer, pulsing action was applied at the base of the column. This was dropped for reasons relating to hydrodynamics and chemical kinetics:

- visual observation of a very high dispersed phase holdup gradient the length of the column, which would require implementing relatively low pulsation and through-put (amplitude × frequency < 1 cm/s and total specific flow-rate < 10 m^3/h·m^2) so as to avoid local flooding, which would result in phase inversion. For example, in the middle of a glass column of 15 mm in diameter and 2 m in height, packed with extruded rods, the evolution curve the dispersed MiBK holdup in water vs. pulsation velocity corresponded to a mixer–settler operating type at amplitude × frequency ranging from 0.2 to 0.8 cm/s. At the bottom of the column, however, fine emulsion was observed at amplitude × frequency = 0.49 cm/s; above amplitude × frequency = 0.67 cm/s, local flooding occurred:
- formation, from the sugars or the HMF, of insoluble polymers which are adsorbed on the cat-

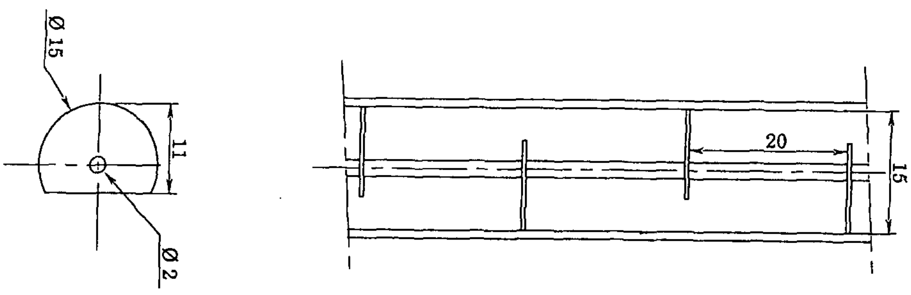

Fig. 1. Hydrodynamic tests: cut disc packing.

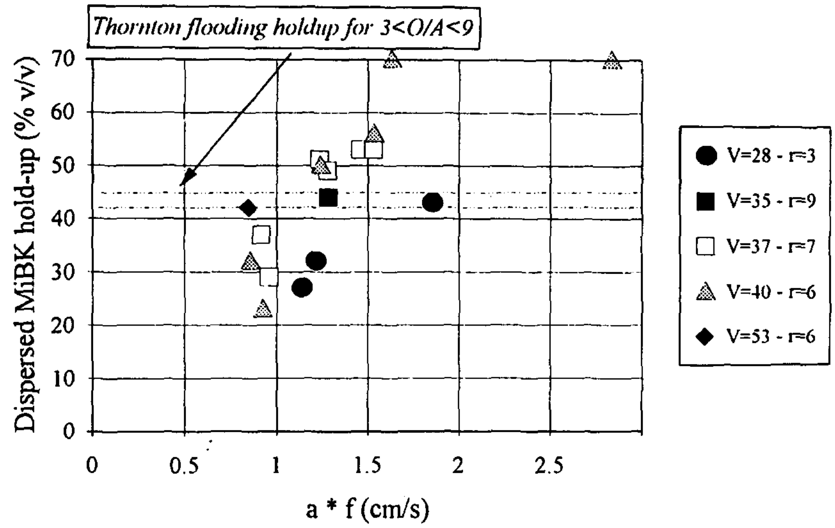

Fig. 2. Hydrodynamic tests: dispersed MiBK holdup (ϵ, % v/v) vs. amplitude–frequency ($a \times f$, cm/s) for different total specific flows (V, m/h) and volumetric flows ratio MiBK/sucrose solution (r).

alyst, causing it to deactivate and disturbing the flow by creating preferential channels;

– impossibility of assembling the zeolite grains in the form of packing known to be efficient in gas–liquid or liquid–liquid extraction, such as the Raschig rings, Berl saddles ...;

– limitation of the chemical kinetics by internal diffusional limitations.

The concern with control of the catalyst circulation and the ability to easily recover it for regeneration was also behind our decision to drop the fixed-bed.

3.2. Reactor–extractor with zeolites in suspension in the reactive aqueous phase

Consequently, we turned to a second type of reactor where the zeolites were in suspension in the aqueous phase, in counter current circulation with a light extracting solvent of the intermediate target component and where the packing is discrete and distinct from the catalyst. This reactor was the subject of research conducted in two stages.

3.2.1. Hydrodynamic tests at 60°C and atmospheric pressure

3.2.1.1. Reactor and operational methodology. The pilot basically consisted of a continuous glass column with an interior diameter of 15 mm and a height of 2 m, outfitted with a double envelope.

The packing — in stainless steel for continuous aqueous phase operation, in PTFE for continuous organic phase operation — consisted of cut discs

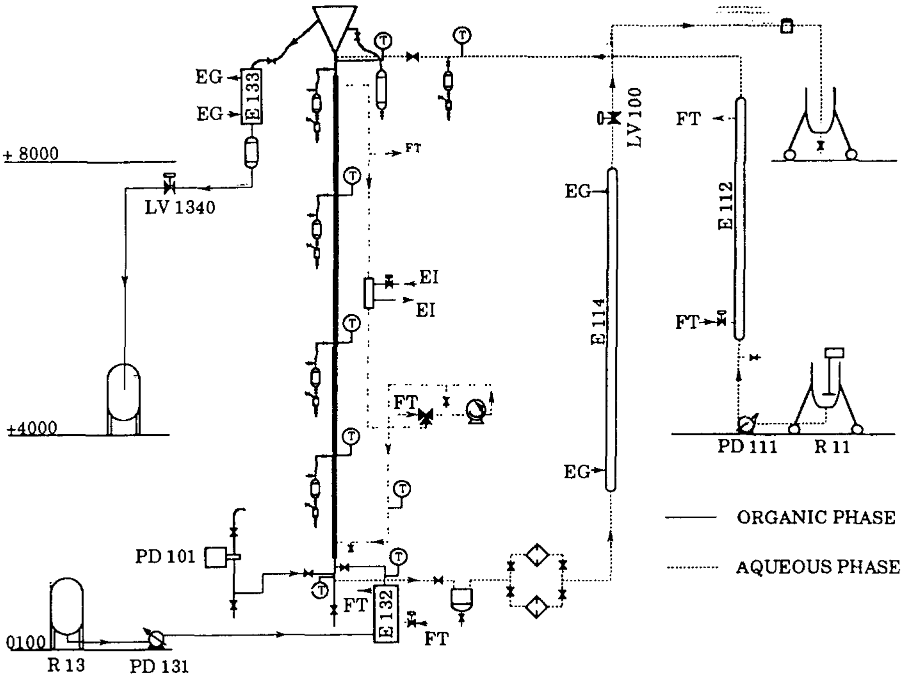

Fig. 3. Chemical tests: schematic diagram of the pilot plant unit.

spaced 20 mm apart with an open free area of 25% (Fig. 1).

The lower settler received the pulsation leg which was connected to a pneumatic pulsator which allowed to adjust the amplitude and the frequency. The heavy aqueous phase contained 200 g sucrose/l and 10 to 50 g/l of zeolites in suspension, the light solvent was methylisobutylketone.

A valve needle was installed in the middle of the column to take samples.

3.2.1.2. Catalysts. The separately tested zeolites were one H-mordenite (Si/Al = 10) with granu-

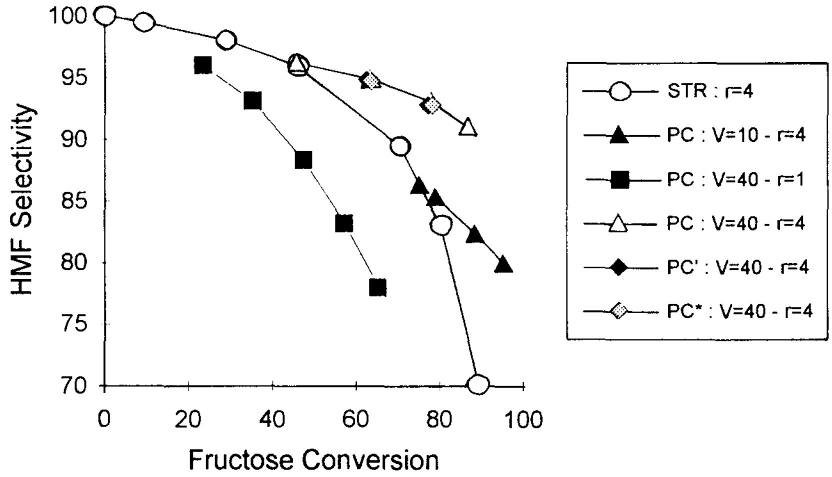

Fig. 4. Simulation: HMF selectivity (s) vs. fructose conversion (c) and $V-r$ (cf. Fig. 1) with identical reaction rate constants in stirred tank reactor (STR) and pulsed column (PC). (Axial dispersion coefficients in continuous and dispersed phase in cm^2/s — PC: $D_c = 10$, $D_d = 10$; PC': $D_c = 20$, $D_d = 10$; PC*: $D_c = 10$, $D_d = 100$).

lometry between 0.5 and 50 μm, and one H-Y faujasite (Si/Al = 15) with granulometry between 0.5 and 20 μm, with a majority between 1 and 4 μm.

3.2.1.3. Analyses. The column hydrodynamic behaviour was assessed by measuring the dispersed phase holdup as a function of the total specific flow-rate, the ratio of phase flow-rates and the stirring conditions. It was determined by taking emulsion samples in a test tube, decantation and measurement of the volumes in each phase.

3.2.1.4. Results and discussion. During operation in the continuous aqueous phase mode, the systems of phases which were tested showed themselves to be extremely efficient from the hydrodynamic standpoint, and enabled large through-put capacities (maximum total specific flow-rate 50 $m^3/h \cdot m^2$) with great flexibility in terms of the flows ratio ($2 <$ organic flow/aqueous flow < 9) as shown for example in Fig. 2.

Dispersed phase holdups that were clearly higher than the holdups at flooding deducted from the Thornton formula [9] were obtained without any flooding and without using high pulsation velocities (amplitude × frequency < 2 cm/s): these observations demonstrate the role of solids in the phenomena of coalescence and drop breakup. Further research is required to correctly explain these phenomena. It was observed that no solid particles were carried into the light phase outlet.

These good hydrodynamic performances are quite interesting in terms of the reaction kinetics in order to break free of the external diffusional limitations to the catalyst grains.

During continuous organic phase mode, maximum pulsation velocity on this pilot plant unit (amplitude = 2.3 cm, frequency = 80 mn^{-1}) did not allow dispersion of the aqueous phase. Research into this operating mode has been temporarily abandoned, since continuous aqueous phase operation is preferable for the first intended industrial applications (dehydration of hexoses), so as to take advantage of a sufficiently long and perfectly controlled residence time of the reaction medium.

3.2.2. Chemical test process

3.2.2.1. Pilot: description and operating principle (Fig. 3). The pilot basically consisted of:

- a stainless steel drum column with inside diameter of 25.5 mm, effective height of 8220 mm, packed with cut stainless steel disks in 25 mm spacing with 25% open free area, maintained under pressure by nitrogen bubbling, with thermoregulation by circulation of heat exchanging fluid — at a slightly higher temperature than the process temperature — in a double envelope; it also contained four sight glasses enabling observation of the emulsion;
- a feed by a membrane dosing pump (PD111) of a hexose solution (R11) with zeolites in suspension; prior to entering the column, the solution is pre-heated in a low dead holdup exchanger (E112);
- a MiBK supply (R13, PD131) preheated (E132) prior to entering the column;
- a heavy phase cooled outlet (E114) regulated by a valve (LV100) which was controlled by the interphase level measurement in the upper settler;
- a light phase outlet by overflow then cooling (E133) and discharge by valve LV1340;
- a mechanical pulsator (PD101);
- sample taking.

3.2.2.2. Analyses. These were identical to the process research.

3.2.2.3. Results and discussion. Tests are still being conducted on the phase system [(water–fructose–mordenite)MiBK] and it is too soon to reach final conclusions on the reaction under study.

However, early results show that use of the ‘average’ conditions established during laboratory tests (fructose concentration = 100 g/l, catalyst concentration = 20 g/l) in the pulsed column can result in eliminating the diffusional limitations.

Furthermore, the CEA has developed software which simulates the liquid–liquid extractions which occur in the nuclear fuel industry. This assumes a plug-flow-dispersion model. It was extended to introduce chemical reactions in one phase.

Simulations performed using this software, based on laboratory-determined kinetics parameters and with a wide range of axial dispersion coefficients, provide results which are in favour of the above-mentioned reactor compared to a continuous stirred slurry reactor in similar conditions, especially equal phase flows ratio (Fig. 4).

These also allow evaluation of the expected strong influence of the ratio of the phase flows and of the total specific flow-rates; the axial dispersion in the continuous and the dispersed phases seems however to play a negligible role.

4. Conclusion

In conclusion, this new S–L–L extractor reactor with zeolites in suspension in the aqueous phase and with simultaneous extraction of an intermediate product of the reaction by means of a solvent circulating countercurrently shows the following advantages:

- both the catalytic activity and molecular sieve properties of the zeolites,
- the superior performances of concentration gradient reactors for positive order chemical reactions,
- the advantages of a countercurrent extractor.

In addition, for its operation, it only requires the usual know how which has been acquired on the liquid–liquid extraction pulsed columns.

For certain applications in the chemistry of sugars, it should allow for component production costs which are compatible with the market demands.

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