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The behaviour of an intermeshing twin screw extruder with catalyst immobilised screws as a three-phase reactor

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Abstract

The characteristics of an intermeshing co-rotating twin screw extruder were investigated as a three-phase reactor using a model reaction. The kinetics of the reaction and base line data were obtained using a high pressure stirred tank reactor. The feasibility of immobilisation of palladium on the surface of the screws as the catalyst was also studied. The behaviour of the extruder in batch and continuous mode and with slurry and non-slurry solutions was investigated. The results confirmed the superiority of the intermeshing co-rotating twin screw extruder as a novel three-phase reactor compared to the stirred tank reactor as a traditional three-phase reactor. The residence time distribution measurements indicated that the behaviour of the extruder approached perfect plug flow reactor with increasing viscosity of reaction solution. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Twin screw extruder; Three-phase reactor; Catalyst immobilisation; Hydrogenation; Mass transfer; Residence time distribution (RTD); Palladium; Viscous solution

1. Introduction

Historically, extruders were first employed as a reactor in the early 1920s for rubber polymerisation and were described in a patent in the 1930s [1]. Some advantages such as excellent dispersive mixing of highly viscous materials, function at high temperatures and pressures, multistaging capability, continuous processing, plug flow reactor behaviour and the capability of intensification of chemical reactions of viscous materials are the main advantages of extruders as chemical reactors [2]. Bulk polymerisation, graft reactions, interchain copolymer formation, crosslinking reactions, controlled degradation and functional group modification of polymers are the most common types of reactions which have been performed successfully by reactive extrusion in polymer industry [3]. A typical example of using reactive extrusion in food industry is extrusion cooking of foods including chemical modification of the starch polysaccharide [4].

The intermeshing co-rotating twin screw extruder is one of the most successful type of extruders used for reactive extrusion because of its self-wiping capability [1]. Most of the studies regarding this kind of reactors have been published in patents and relatively a few open papers have been published till two decades ago [2]. In the recent years it has been one of the important subjects in academia and industry. However, investigations have mainly concerned with one- or two-phase reactions. Recently, Jordi et al. [5] introduced an intermeshing co-rotating twin screw extruder as a continuous reactor for catalytic hydrogenation of soya

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bean oil. Orchard [6] studied the behaviour of the same extruder as a three-phase reactor, however, since soya bean oil is not a viscous solution at high temperatures, the study was limited to the reactions of non-viscous solutions.

In this work, the behaviour of an intermeshing co-rotating twin screw extruder (ICoTSE) was studied as a three-phase reactor for relatively highly viscous solutions. A model reaction was chosen for this purpose and the base line results were obtained using a stirred tank reactor (STR) as a conventional reactor. The ICoTSE was operated batchwise and continuously and its behaviour was compared with the STR. Palladium as the catalyst was immobilised on the surface of the screws to eliminate the catalyst separation stage which is a costly and time consuming stage. Since no generally satisfactory studies of residence time distribution and mixing in intermeshing co-rotating twin screw extruder have been available [1] this parameter was investigated.

2. Experimental

2.1. Model reaction

The catalytic hydrogenation of dimethyl itaconate (DMI) in the presence of a palladium catalyst was chosen as a model reaction. A type of carboxy methyl cellulose (CMC) was added into the solutions to increase the viscosity of the solutions. The solvent was a mixture of water and propan-2-ol. The catalyst in slurry reaction was a 5 wt% Pd/C and in non-slurry reactions palladium was immobilised on the surface of impellers in the STR or screws in the ICoTSE.

2.2. High pressure stirred tank reactor (STR)

Preliminary experiments were carried out in a 500 cm^3 stainless steel autoclave to study the kinetics of the model reaction and collect some base line data for further comparison. The autoclave was equipped with a mechanical stirrer and fitted with four standard baffles. It was operated as a dead-end reactor and hydrogen was introduced into the reactor by a hydrogenation control unit. The rate of hydrogen consumption was recorded by a chart recorder as the representative of the reaction rate. The most important parameters in these experiments were initial concentration of DMI, partial pressure of hydrogen, catalyst loading and viscosity of the solution. Table 1 shows the reaction conditions.

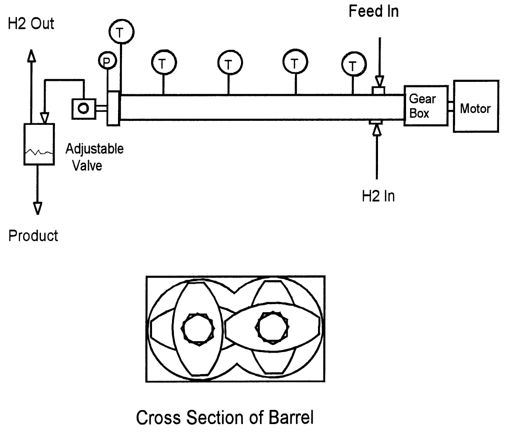
2.3. Intermeshing co-rotating twin screw extruder (ICoTSE)

A 16 mm intermeshing co-rotating twin screw extruder was used as a novel reactor for three-phase reactions. The working length to diameter was 20 to 1. The barrel was made from stainless steel and its cross section was of the "figure 8" shape. The screws were two series of right angle paddles. They were a pair of shafts with a number of semi-elliptical shaped paddles on each of these shafts. The paddles were at right angles to each other on their individual shafts and also at right angles to the corresponding paddles on the other shaft. Since the screws were intermeshing, the paddles could thoroughly wipe each other without contacting each other and the fresh surface of immobilised catalyst contacts with the reactants when non-slurry solution is used. The schematic diagram of the extruder and its specifications are shown in Fig. 1. Hydrogen was introduced into the reactor from underneath of the barrel exactly to the opposite of liquid entrance. The solution was pumped into the barrel using a positive displacement pump. The solution contained very fine particles of Pd/C catalyst in slurry reactions. The pressure inside the barrel was adjusted using a variable pressure relief valve that could manually be adjusted during operation.

Table 1
Reaction conditions in STR and ICoTSE

	C_0 (kg m^{-3})	W_C (kg m^{-3})	V_R (dm^3)	μ_a (cp)	N_s (s^{-1})	T (°C)	P_{H_2} (10^5 Pa)
STR	10–50	0.5–3.0	0.200	1–570	16.7–20	25–65	1–11
ICoTSE	30	0.5–2.0	0.016–0.056	1–4530	0.8–4.7	35–85	8–40

[a] It is the viscosity of a solution with 0.0–1.5% (w/w) and 0.0–3.0% (w/w) CMC concentration, respectively.



Extruder Specifications:

Type: Intermeshing Co-rotating Twin Screw Extruder
Screws: Right Angle Paddles
Cross Section of Barrel: '8' Shape
Length to Diameter: 20/1
Working Length: 256 mm
Diameter: 16 mm

Fig. 1. Schematic diagram and specifications of the ICoTSE.

The experiments with slurry solutions and batch operation were performed to compare the behaviour of the ICoTSE as a novel reactor with the STR as a conventional reactor. In these experiments hydrogen was supplied by the same hydrogenation control unit and the reaction rate was calculated using hydrogen consumption during the reaction. In continuous operation, some samples were taken and analysed using a gas chromatograph.

To eliminate the problems of working with slurry reactions and disadvantages associated with catalyst separation, palladium was immobilised on the surface of the screws. The details of the experiments for immobilised palladium were mentioned elsewhere [7]. The most important factors for the study of the ICoTSE under these conditions included volume of the solution in the barrel, rotational screw speed, catalyst loading, temperature and viscosity. The reaction conditions are listed in Table 1.

2.4. RTD measurements

To determine the characteristics of the ICoTSE as a continuous reactor, some RTD measurements were performed. A 20 g l^{-1} potassium chloride (KCl) solution was used as a tracer and it was injected into the reactor exactly above the entrance of the barrel. The concentration of KCl in the samples taken from the outlet was measured using a conductivity meter. Liquid flow rate, rotational screw speed and viscosity of the solution were the most important variables studied. The maximum concentration of CMC used in the solution was chosen to be 2% (w/w) because the feed pump could not pump the solutions with more than this amount of CMC.

3. Results and discussion

3.1. Reaction kinetics studies

The initial reaction rates of hydrogenation of DMI (without adding any CMC) in the presence of a 5 wt% Pd/C in the STR were used to study the reaction kinetics. The stirrer speed was adjusted at 1000 rpm to eliminate gas absorption mass transfer resistances. The results indicated that the reaction was first-order and zero-order with respect to the partial pressure of hydrogen and initial concentration of DMI, respectively, under the reaction conditions. The reaction rate increased linearly by increasing catalyst loading up to 2 g l^{-1} which confirmed the absence of gas–liquid mass transfer resistance. Hence, the reaction equation can be expressed as follows:

$$R_A = k' P_{H_2}^1, \tag{1}$$

where

$$k' = k_r W_C^1 C_{DMI}^0. \tag{2}$$

3.2. Effect of viscosity on reaction rate

Some experiments were carried out in the STR and ICoTSE under the same conditions to study the performance of the reactors when the viscosity of the reaction solution increases. The reaction rate in the STR was 9.6 mol m^{-3} s^{-1} at 25°C and 1050 kPa which was obviously higher than that in the ICoTSE when no CMC added to the reaction solution. How-

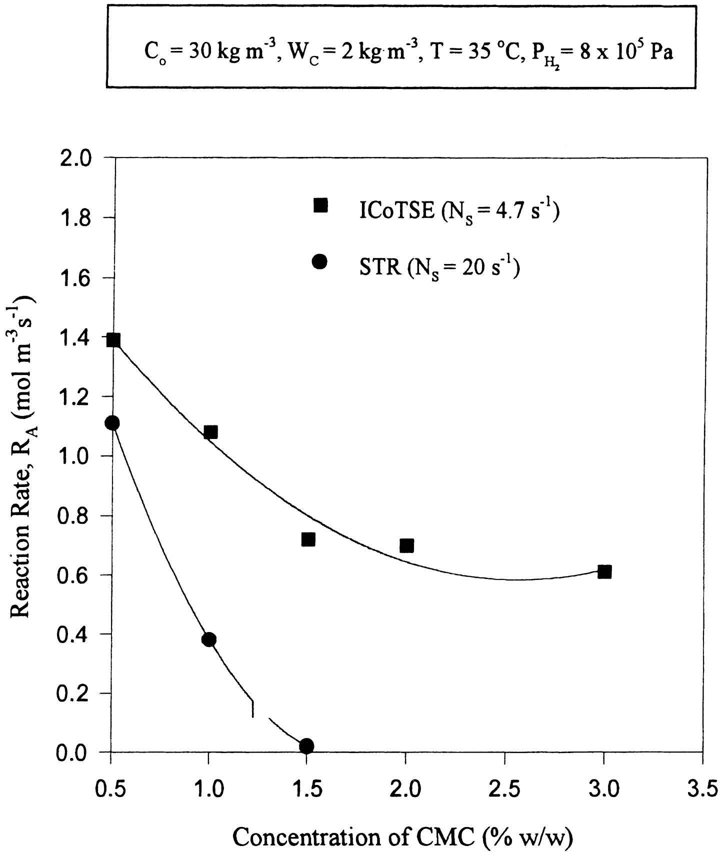


Fig. 2. The effect of viscosity on reaction rate in ICoTSE and STR.

ever, with increasing viscosity of the solution, the reaction rate in the STR sharply decreased and became nearly zero for a 1.5% (w/w) CMC solution. The main reason for that was the lack of turbulence on the surface of the liquid and poor mass transfer coefficients in the STR. The reaction rate in the ICoTSE was decreased slightly with increasing viscosity and it approached a constant level beyond a 1.5% (w/w) solution. This is because of effective mixing of viscous solutions in the ICoTSE and self-wiping characteristics of intermeshing extruder, especially when it works in starved (see Section 3.4) mode. Fig. 2 shows the results for the STR and ICoTSE.

3.3. Gas–liquid mass transfer

Volumetric gas–liquid mass transfer coefficient, k_La, in the STR and ICoTSE can be determined using classical film model for first-order reactions [8]:

$$\frac{C^*}{R_A}=\frac{1}{k_La}+\frac{\rho_P d_P}{6W_C}\left\{\frac{1}{k_s}+\frac{1}{\eta k_r}\right\}. \tag{3}$$

Fig. 3 shows that under the mentioned reaction conditions $1/R_A$ was almost independent of $1/W_C$ indicating the reaction rates in both reactors were under gas–liquid absorption mass transfer control [9]. Since the solubility of hydrogen in the CMC solution is almost constant below a concentration of 2% [10], k_La was calculated using the value of the solubility of hydrogen in the solvent without CMC. The volumetric gas–liquid mass transfer coefficient was found to be 0.072–0.196 s^{-1} in the STR when the concentration of CMC was 0.5–1% (w/w), but it was 0.9–2.1 s^{-1} in the ICoTSE for 0.5–2.0% (w/w) CMC solutions.

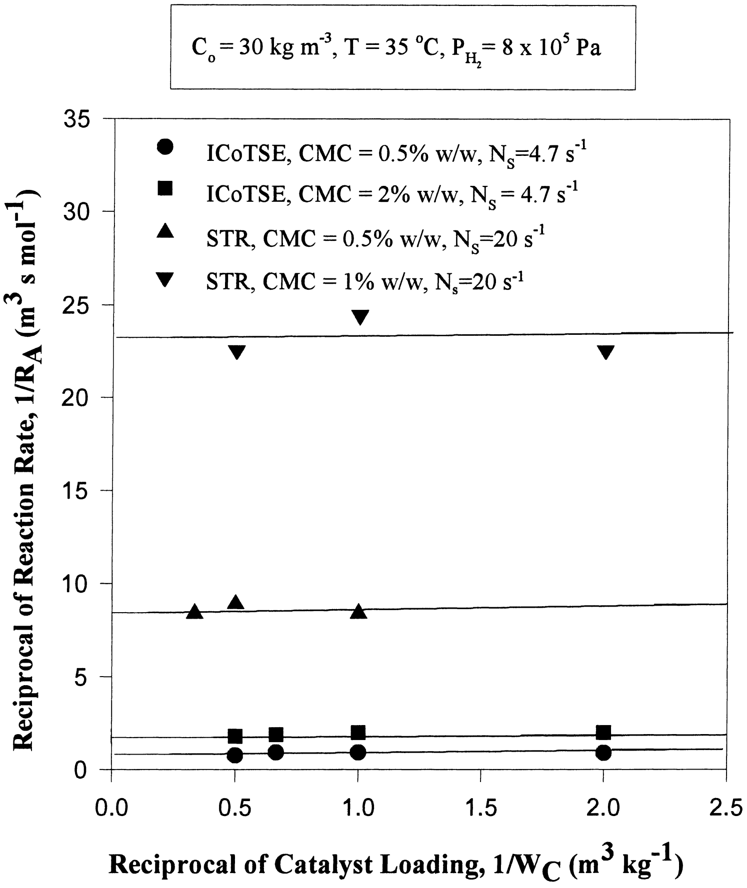


Fig. 3. Comparison of k_La in ICoTSE and STR.

The values of gas–liquid mass transfer coefficients in the reactors highlighted the superiority of the ICoTSE compared to the STR for highly viscous solutions.

3.4. Important parameters in ICoTSE

One of the most important factors on the performance of the ICoTSE was the volume of the solution in the barrel. It was found that in partially filled barrel (starved mode) the reaction rate was much higher than completely filled barrel. The reaction rate against volume of the solution in the barrel is plotted in Fig. 4(a). It indicates that the contact between the phases became poor with increasing the volume of the solution. However, if the volume of the solution became less than a certain value, the reaction rate would decrease. An intermediate amount (about 35 cm^3) of the solution was introduced into the barrel in the rest of batch experiments to give the maximum hydrogen uptake (Fig. 4(b)) although the reaction rate was higher for smaller amounts of solution in the barrel.

The other important factor was found to be rotational screw speed. Fig. 5 shows that the reaction rate increases with increasing rotational screw speed depending on the temperature and viscosity of the solution. At higher temperatures and lower concentration of CMC, the effect of rotational screw speed was greater.

One of the important factor in three-phase reactors is gas hold-up, however, since the barrel was made from stainless steel it was not possible to study this parameter in the ICoTSE, i.e. using visual observations.

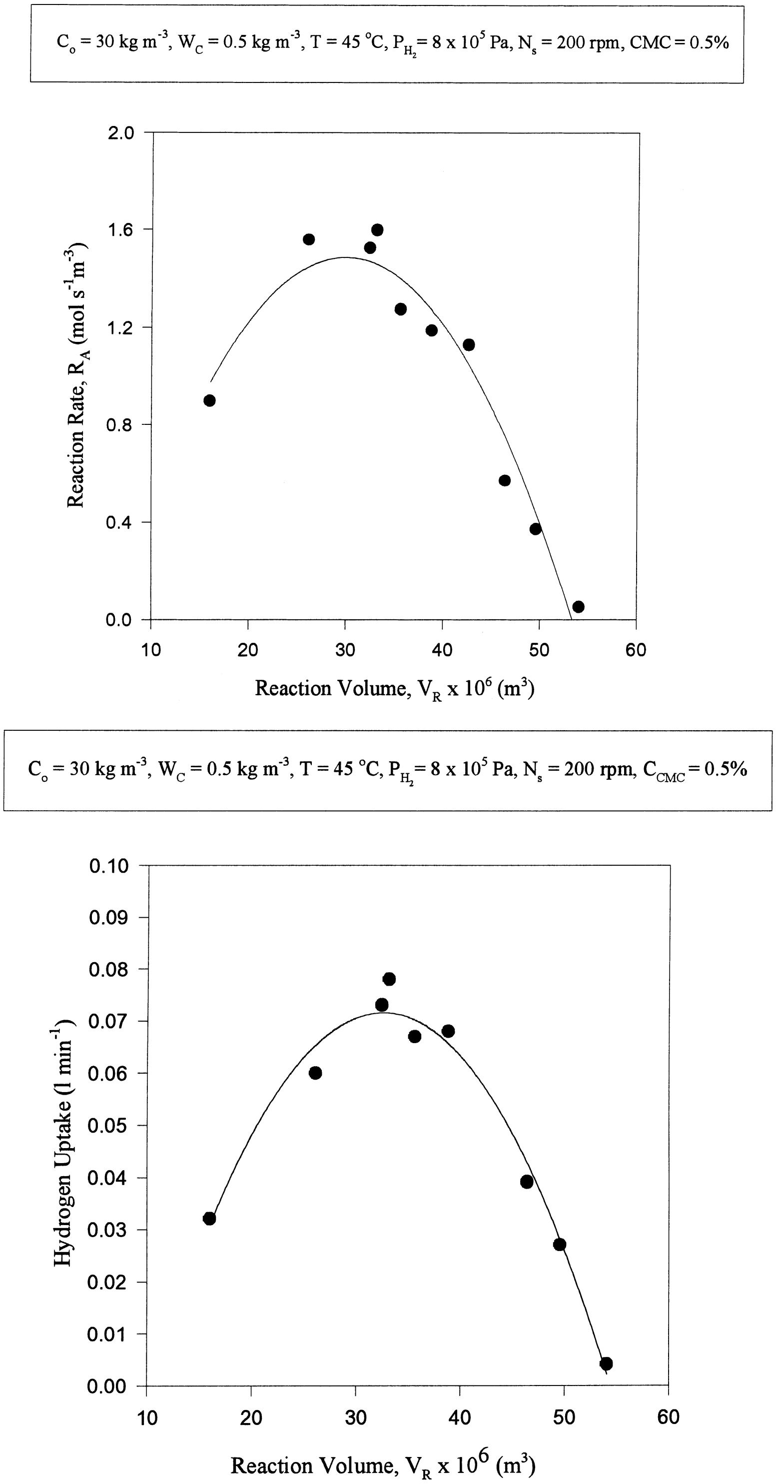


Fig. 4. (a) The effect of volume of solution in barrel on reaction rate. (b) The effect of volume of solution in barrel on hydrogen uptake.

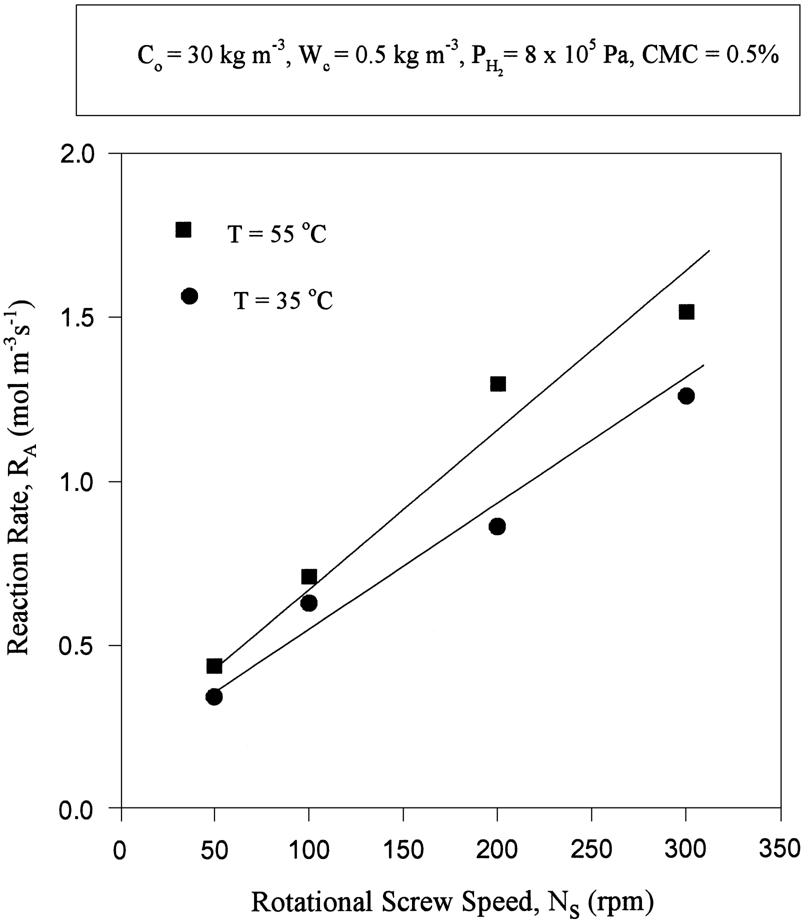


Fig. 5. The effect of rotational screw speed on reaction rate.

3.5. ICoTSE with immobilised catalyst on the screws

To investigate the feasibility of using an immobilised catalyst in the ICoTSE, firstly the optimum conditions of palladium immobilisation were established [7]. The optimum method was found to be a thin layer of alumina using plasma spray followed by a palladium electroless coating. The alumina powder used was an α-alumina and the composition of the alumina sprayed was found to be a mixture of α- and γ-alumina.

The optimum method was employed to immobilise palladium on the surface of the screws. The initial reaction rates obtained with immobilised catalyst were comparable with those obtained in the slurry solutions and when the reaction rates were calculated based on catalyst surface area, they were much greater in value than those evaluated for slurry operation.

General trends indicated that the initial reaction rates for the immobilised catalyst experiments showed the same dependency on rotational speed of screws, viscosity of the solution and temperature as determined under slurry operation. The activity of the immobilised catalyst was maintained beyond 35 experiments, covering two weeks operation, indicating the possible durability of the optimum catalyst surface, but no extended tests were possible. It should be pointed out that Orchard [6] observed a similar durability for an immobilised Pd catalyst for soya bean oil hydrogenation in the same unit.

In continuous operation with the immobilised catalyst, the main variable parameters were the mode of introducing hydrogen into the barrel, partial pressure of hydrogen and temperature. The initial reaction rate and conversion in this part of work were determined using gas chromatograph analysis. The mode of introducing hydrogen was found to be essential operational parameter. When an excess amount of hydrogen was continuously introduced into the barrel, the product exited unevenly from the reactor. To have a uniform flow in the extruder, the amount of hydrogen introduced into the barrel should precisely be controlled. In this case, the effluent was a continuous flow of the solution containing fully dispersed small bubbles of hydrogen. Although the reaction rate was found to be greater in the case of introducing an excess amount of hydrogen continuously, the second method was found to be more suitable for a stable continuous operation.

The reaction rate increased with increasing temperature. That is because of the combination of decreasing viscosity of the solution and the increasing rate of controlling step. In one series of experiments with 2 g l^{-1} initial concentration of DMI and 4 MPa partial pressure of hydrogen, the conversion increased from 37.4% to 54.7% when temperature increased from 35°C to 85°C. The reaction rate increased with the increasing partial pressure of hydrogen because of increasing the concentration of hydrogen in the solution.

The results showed the possibility of obtaining a reasonable conversion (more than 50%) in one pass of the solution through a 256 mm reaction zone in the barrel with the immobilised catalyst. The study of durability of the immobilised catalyst indicated that in continuous operation, the activity of the catalyst remained nearly constant for a longer time compared to that for batch operation. The reason is probably due to the lack of contact of the catalyst surface with air in continuous operation.

3.6. *RTD measurements*

The characteristics of ICoTSE continuous operation was determined by studying the residence time distribution (RTD) in the extruder [11]. Summary of the results including mean residence time (t_m), variance (σ^2) and Peclet number (Pe_r) are listed in Table 2. As seen in Table 2 Peclet number increased with increasing viscosity of the solutions and using higher rotational screw speed. Since Pe_r is proportional to reciprocal of the axial dispersion coefficient of liquid phase (D), therefore, the intensity of the axial dispersion would decrease under these conditions and consequently the behaviour of the ICoTSE approached perfect flow reactor. The Peclet numbers obtained from RTD measurements can be used for modelling the reactor in future work.

Table 2
Mean residence time, variance and Peclet number for ICoTSE

CMC (%, w/w)	v_L (cm^3 min^{-1})	t_m (s)	σ^2 (s^2)	Pe_r
0	43	119.1	2446	10.5
	114	48.6	823	7.2
	225	28.4	160	9.0
1	43	143.5	2325	16.7
	114	55.5	546	10.2
	225	25.3	97	12.1
2	43	124.7	696	43.7
	114	49.4	157	30.0
	225	23.6	33	33.1

4. Conclusions

The following conclusions can be drawn from the present work.

1. The catalytic hydrogenation of dimethyl itaconate on a Pd catalyst was found to be a first-order in partial pressure of hydrogen and zero-order with respect to initial concentration of dimethyl itaconate.
2. The overall reaction rate in the intermeshing co-rotating twin screw extruder and stirred tank reactor was under gas–liquid mass transfer control when viscosity of the reaction solution was relatively high, the volumetric gas–liquid mass transfer coefficient for the extruder was more than 10 times greater than that of the stirred tank reactor.
3. The reaction rate in the extruder was higher when the barrel was starved.
4. The reaction rate in the extruder increased with increasing rotational screw speed depending on

temperature and viscosity of the solution. At higher temperature and lower concentration of CMC in the solution, the effect of this parameter was greater.

5. In continuous operation of the extruder, the method of introducing hydrogen was one of the most important variable parameters.
6. A conversion of more than 50% was obtained with the immobilised catalyst in the extruder in a short length of reaction zone.
7. The feasibility of using an intermeshing co-rotating twin screw extruder with immobilised catalyst on the screws as a three-phase reactor was demonstrated.

5. Nomenclature

C^*	equilibrium concentration of hydrogen ($mol\ m^{-3}$)
C_0	initial concentration of liquid reactant ($mol\ m^{-3}$)
C_{DMI}	concentration of liquid reactant ($mol\ m^{-3}$)
D	axial dispersion coefficient of liquid phase ($m^2\ s^{-1}$)
d_p	average diameter of catalyst particles (m)
k'	first-order reaction constant ($mol\ m^{-3}\ s^{-1}\ Pa^{-1}$)
k_r	surface reaction constant ($mol\ kg^{-1}\ Pa^{-1}\ s^{-1}$)
k_s	liquid–solid mass transfer coefficient ($m\ s^{-1}$)
k_La	volumetric gas–liquid mass transfer coefficient (s^{-1})
N_s	screw/stirrer speed (s^{-1})
P_{H_2}	partial pressure of Hydrogen (Pa)
Pe_r	Peclet number (dimensionless)
R_A	reaction rate ($mol\ m^{-3}\ s^{-1}$)
T	temperature (°C)
t_m	mean residence time (s)
v_L	liquid flow rate ($cm^{-3}\ min^{-1}$)
V_R	volume of solution in reactor (dm^3)
W_C	catalyst loading ($kg\ m^{-3}$)
σ^2	variance (s^2)
ρ_p	catalyst density ($kg\ m^{-3}$)
μ_a	apparent viscosity (cp)

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