

Effect of reaction engineering factors on biphasic hydroformylation of 1-dodecene catalyzed by water-soluble rhodium complex

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Abstract

Hydroformylation of 1-dodecene in a biphasic system using water-soluble rhodium catalyst $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ [TPPTS: tri(sodium-*m*-sulfonatophenyl) phosphine] was investigated. The cationic surfactant cetyltrimethyl ammonium bromide (CTAB) was used to enhance the reaction rate of long chain olefin and the ratio of normal/isomeric aldehyde. Experiments were carried out semi-batchwise in a 500 ml stirred autoclave at 100 °C and 1.1 MPa. An orthogonal experimental design was adopted for analyzing the effects of agitation intensity, 1-dodecene concentration, surfactant concentration and organic/water volume ratio on the macro-kinetics and regioselectivity. Several agitation configurations for improving the mixing, dispersion and interphase mass transfer of this gas–liquid–liquid reaction system were tested and higher hydroformylation rate and regioselectivity were achieved. The relationship between the extent of emulsification of reaction mixture and the performance of hydroformylation reaction was also studied. Empirical macro-kinetic equations for the initial rate and the correlation of normal/isomeric aldehyde ratio are proposed, which represented the experimental data reasonably well.

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1. Introduction

The biphasic hydroformylation of olefins catalyzed by water-soluble rhodium complexes has attracted great attention in recent years for its easy and efficient separation of catalyst from products by simple decantation. Although industrial homogeneous hydroformylation has been applied to long chain olefins, the environmental benign, safe and economical biphasic process has so far only been applied to propylene (Ruhrchemie/Rhône-Poulenc process) [1,2] and butylene [3], which have significant water solubility. For long chain substrates, e.g. 1-dodecene with low

solubility in the aqueous phase, the rate of biphasic reaction is governed mainly by the interphase mass transfer between the organic and aqueous phases. Therefore many efforts have been devoted during the last several years either to develop novel active metal complex catalysts and ligands [4,5] or to improve the miscibility and solubility of reactants, mainly by using amphiphilic ligands [6–8], co-ligands [9,10], cyclodextrins [11,12] and supported aqueous phase catalysts (SAPC) [13,14], or by adding solvents or co-solvents [15–17] and surfactants [18–22].

The addition of surface-active agents such as cetyltrimethyl ammonium bromide (CTAB) to biphasic hydroformylation system forms micelle or microemulsion with continuous and dispersed phases. It could induce enrichment of rhodium catalyst in the

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Nomenclature

A_0	pre-exponential factor of kinetic model
C	concentration of various component (kmol/m ³)
k_1 – k_4	constants in kinetic model equation
n/i	ratio of normal/isomeric aldehyde
N	agitation speed (rpm)
p	total pressure (MPa)
P	power consumption of motor (W)
r	initial rate of hydroformylation reaction (kmol/m ³ /s)
T	reaction temperature (°C)
V_O/V_W	volume ratio of organic/aqueous phase
x	conversion of olefin
y	molar fraction of gas component

Subscripts

cal	predicted values by kinetic models
cat	rhodium complex catalyst
CO	carbon monoxide
CTAB	cetyltrimethyl ammonium bromide
d	1-dodecene
exp	observed values by experiments
H ₂	hydrogen
lig	ligand TPPTS
L	total liquid phase based
O	organic phase based

Greek letter

ϕ	sum of square of errors between calculated and experimental
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interfacial layer through static electricity interaction [19], so the catalyst coordinates more easily with reactants dissolved in micelles. Although the formation of relatively stable emulsion makes the gravity phase separation difficult in such a system, high activity and regioselectivity and much low ligand costs for the hydroformylation of higher olefins render it attractive and feasible for potential commercialization.

Biphasic hydroformylation is a typical and complicated gas–liquid–liquid reaction. Although extensive studies on catalysts, ligands and catalytic product distributions have appeared, the reaction mechanism has not been understood sufficiently and even

contradictory concepts on the site of hydroformylation reaction were developed [9,10,23]. When surfactants were added to accelerate the catalytic reaction, the performance indicated that the biphasic reaction might occur mainly in the interface of aqueous–organic phases instead of the bulk of the liquid mixture [19,24]. Up to now only limited data are available for the kinetics of biphasic hydroformylation reactions and the chemical reaction engineering. The kinetics of low carbon olefins, ethylene [25] and propylene [26], in aqueous systems were reported and different rate models proposed. The biphasic hydroformylation of 1-octene was studied in the presence of ethanol as a co-solvent and a proposed kinetic rate expression was nearly identical to that of the homogeneous system [16,27]. A further modeling of this biphasic hydroformylation system was conducted by Lekhal et al. [28] to analyze the experimental data by coupling kinetics to a pseudo-homogeneous gas–liquid–liquid macroscopic conservation model, and the authors proved that gas–liquid mass transfer was the only limitation. Zhang et al. [21,22] investigated the macro-kinetics of 1-dodecene hydroformylation catalyzed by RhCl(CO)(TPPTS)₂ [TPPTS: tri(sodium-*m*-sulfonatophenyl) phosphine] complex in the presence of CTAB and analyzed the influence of interphase mass transfer by computational fluid dynamics method. Wachsen et al. [23] proved that aqueous biphasic hydroformylation of propylene took place at the interfacial region, in contrast to two preliminary kinetic models that incorporate mass transport.

In practice, to perform gas–liquid–liquid hydroformylation reactions in a multiphase reactor is necessary to combine intrinsic kinetics, mass and heat transfer, residence time distribution and reactor configuration in an appropriate mathematical model. It is not only instructive for improvement of the catalytic complexes and ligands but also provides the basic information for design and scale-up of novel industrial reactors for hydroformylation of higher olefins. The mass transfer resistance depends largely on the solubility of reactants, thermodynamic phase equilibrium, permeability, interfacial properties, as well as the hydrodynamics of gas–liquid–liquid dispersion and mixing. Previous studies [19,21,29,30] indicated that the intensity and mode of stirring and reactor configuration affected dramatically the reaction rate and selectivity of biphasic hydroformylation of

1-dodecene catalyzed by water-soluble complexes. In this paper, the effects of several pivotal reaction engineering factors including agitation intensity, reactor configuration and reaction technological conditions on hydroformylation of 1-dodecene as a typical higher olefin using $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ complex catalyst and cationic surfactant will be reported, and from the data the overall kinetics and mechanism of the concerned multiphase reaction will be derived, which is also the central topic of research and development work on multiphase reaction systems.

2. Experimental

2.1. Chemicals

The water-soluble ligand TPPTS and the rhodium catalyst precursor $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ were provided by Sichuan University, China [31,32]. 1-Dodecene (Fluka), *n*-decane and CTAB (AR) were used without further purification. Hydrogen ($\geq 99.99\%$) and carbon monoxide ($\geq 99.99\%$) were purchased from Huayuan Gas Chemical Industry, China and mixed as syngas with the specified H_2/CO molar ratio of 48.3/51.7. The syngas was then purified by passing through dehydration, decarbonylation, desulfurization and de-oxidation columns prior to use. De-ionized water was used in all experimental runs.

2.2. Experimental setup and procedure

Hydroformylation of 1-dodecene was carried out in a 500 ml stirred stainless steel autoclave (Fig. 1) with an internal diameter of 65 mm. The reactor was equipped with a pressure transducer-monitor system and an automatic temperature control system consisting of an external electric heating jacket and an internal cooling coil. The pressure could be maintained within ± 1 kPa and the temperature within ± 1 °C.

As shown in Fig. 1, the stirrers adopted in this work included two types, i.e. standard Rushton disk turbine (DT) with six blades and pitched blade turbine upward (PBTU) with six blades, and 36 mm in diameter. The DT and PBTU were used as surface aerators for entraining gas reactants into the liquid solution phases and for avoiding the recovery, recompression and recycle of unreacted gases. A self-made

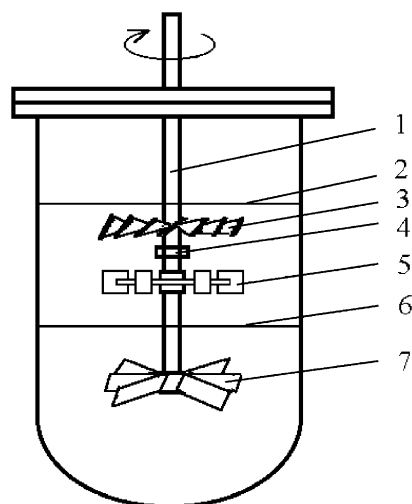


Fig. 1. Hydroformylation autoclave with a composite surface aeration configuration: (1) shaft; (2) gas/liquid interface; (3) SRFB; (4) annulus for position limiting; (5) standard Rushton DT; (6) liquid/liquid interface; (7) PBTU.

baffle named self-rotating floating baffle (SRFB) [33] was also applied for improvement of gas and liquid dispersion and pumping capability. The SRFB was 36 mm in diameter and made from a circular stainless steel sheet with thickness of 0.2 mm. A central hole was made for fitting it around the shaft so as to rotate and float freely around the shaft. The sheet was cut radially to form 12 fan blades and each was twisted by 30° angle to the horizontal plane to ensure the baffle remained afloat over the surface aerator as impinged by the swirling stream discharged from the impeller.

In a typical experimental run, dissolved $\text{RhCl}(\text{CO})(\text{TPPTS})_2$, TPPTS and CTAB with required amounts were charged into the reactor. The organic phase of 1-dodecene and the diluent *n*-decane (if needed) were then added to make the total liquid volume 200 ml. The autoclave was evacuated and purged with nitrogen and syngas successively, and then heated to the desired temperature. After that, the reactor was charged with syngas of CO and H_2 to a desired total pressure of 1.1 MPa and kept constant during a whole run. The above-mentioned procedures were done at very low agitation speed to ensure that no reaction took place up to this point. The hydroformylation reaction conducted in a semi-batch mode was allowed to start by increasing agitation speed to the specified rate.

Liquid samples (each less than 2 ml) were withdrawn at regular time intervals and analyzed using a gas chromatograph.

2.3. Power of agitation

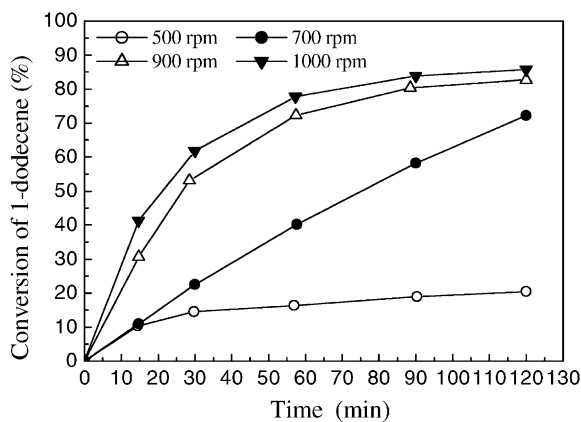
The power consumption of the reactor stirrer is one of the key factors for characterizing the gas–liquid–liquid flow, dispersion and mass transfer and energy efficiency. Since the preliminary experiment [34] showed that the pulsation of the direct-current motor might damage the A/D board for direct acquisition of data on the working current and voltage from the motor, a current transducer and a voltage transducer (Kehai, China) based on the Hall effect and magnetic compensation were incorporated to determine the power consumption of the stirrer motor. The output signal was collected through a SC-11150 A/D board into a personal computer and processed. The efficiency of the direct-current motor was taken as 85% while adjusting the armature voltage to modulate agitation speed. The net power for agitating the reaction mixture was corrected by subtracting the power consumed for driving the stirrer shaft with no liquid phase loaded.

3. Results and discussion

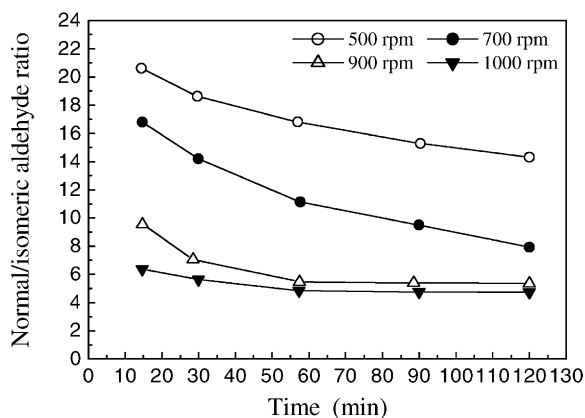
The molar ratio of hydrogen to carbon monoxide was chosen close to 1/1 (48.3/51.7). No hydrogenation or isomerization of alkene were observed within the range of reaction conditions covered in this paper. The experimental repeatability of the concerned hydroformylation reactions was excellent, and the relative deviations of the determined conversion and normal/isomeric aldehyde ratio of two runs with the same conditions were found to be below 4%.

3.1. Effect of agitation speed

The influence of agitation speed on the initial rate, conversion and normal/isomeric aldehyde ratio of biphasic hydroformylation of 1-dodecene was investigated in preliminary runs. As shown in Fig. 2 and Table 1, the initial rate and conversion increased with the agitation speed, but the regioselectivity to *n*-tridecyl aldehyde decreased. These data demonstrated that violent stirring was unfavorable for the



(a) Conversion of 1-dodecene



(b) Normal/isomeric aldehyde ratio

Fig. 2. Influence of agitation speed on the conversion and regioselectivity of 1-dodecene hydroformylation. Reaction conditions: $T = 100\text{ }^{\circ}\text{C}$, $p = 1.1\text{ MPa}$, $V_{\text{O}}/V_{\text{W}} = 3/7$, $y_{\text{H}_2}/y_{\text{CO}} = 48.3/51.7$, $C_{\text{cat}} = 1.5 \times 10^{-3}\text{ kmol/m}^3$, $C_{\text{d}} = 4.4\text{ kmol/m}^3$ (60 ml 1-dodecene), $C_{\text{CTAB}} = 11.0 \times 10^{-3}\text{ kmol/m}^3$, $C_{\text{lig}}/C_{\text{cat}} = 18$, PBTU (stirrer): (a) conversion of 1-dodecene; (b) normal/isomeric aldehyde ratio.

formation of linear aldehyde in the presence of cationic surfactant CTAB. The probable reason was the orderly micelle microstructure at aqueous–organic phase interface was disturbed by stirring [19,34]. Although the hydroformylation rate still increased slightly at high enough agitation speed, the mass transfer resistance for reactants and catalyst beyond 900 rpm was considered negligible in comparison with the intrinsic kinetics.

Table 1
Biphasic hydroformylation of 1-dodecene at different agitation speeds^a

<i>N</i> (rpm)	$r_L \times 10^3$ (kmol/m ³ /s)	$r_O \times 10^3$ (kmol/m ³ /s)	n/i^b	x (%) ^b	<i>P</i> (W)
500	0.0577	0.192	14.3	20.5	0.18
700	0.168	0.560	7.93	72.2	0.41
900	0.383	1.28	5.35	82.7	1.12
1000	0.406	1.35	4.74	85.8	1.47

^a Reaction conditions are the same as in Fig. 2.

^b Observed values after 2 h reaction time.

3.2. Orthogonal experimental design

Besides the pronounced effect of stirring intensity, a number of factors such as pressure, reactant and catalyst concentrations, and temperature will affect the biphasic hydroformylation of 1-dodecene since it is a gas–liquid–liquid three-phase reaction with a complicated reaction mechanism. In a previous research [21], the effects of temperature, total pressure, H₂/CO molar ratio, catalyst and ligand concentration, olefin concentration, surfactant concentration and volume ratio of organic to aqueous phase on hydroformylation kinetics were studied. The preliminary optimal reaction conditions were found to be $T = 100$ °C, $p = 1.1$ MPa,

$V_O/V_W = 3/7$, $y_{H_2}/y_{CO} = 1/1$, $C_{cat} = 1.5 \times 10^{-3}$ kmol/m³, $C_{lig}/C_{cat} = 18$, $C_d = 2.2$ kmol/m³ and $C_{CTAB} = 11.0 \times 10^{-3}$ kmol/m³ from orthogonal experiments. In this work, an orthogonal experimental design was conducted to further investigate some pivotal reaction engineering parameters, which exerted strong influence on the conversion and regioselectivity of biphasic hydroformylation, especially when surfactants were added to the biphasic system.

As listed in Table 2, an orthogonal table of $L_{12}(3^1 \times 2^4)$ was adopted to examine five variables: agitation speed, CTAB concentration, 1-dodecene concentration, agitating stirrer type and the volume ratio of organic/aqueous phase at different levels. The observed initial rate, conversion, regioselectivity and power consumption varied remarkably with different parameters, suggesting that the optimization of reaction engineering conditions for improving productivity, selectivity and energy efficiency is a significant techno-economical necessity.

The relative importance of factors to process indexes and the optimal set of factor levels were determined by margin and variance analysis according to the results shown in Table 2. The order of importance of the investigated factors corresponding to the maximum initial rate, normal/isomeric aldehyde ratio and

Table 2
Orthogonal table of $L_{12}(3^1 \times 2^4)$ for experimental design and the experimental results^a

No.	<i>N</i> (rpm)	V_O/V_W	$C_{CTAB} \times 10^3$ (kmol/m ³)	Stirrer type	C_d (kmol/m ³)	$r_L \times 10^3$ (kmol/m ³ /s) ^b	$r_O \times 10^3$ (kmol/m ³ /s) ^b	n/i^c	x^c (%)	<i>P</i> (W)
1	1 (500) ^d	1 (3/7)	1 (11.0)	2 (PBTU)	2 (4.4)	0.0577	0.192	14.3	20.5	0.18
2	1	2 (1/1)	1	2	1 (2.2) ^e	0.0393	0.079	8.71	37.2	0.10
3	1	1	2 (12.3)	1 (DT)	1	0.0262	0.087	12.7	57.8	0.20
4	1	2	2	1	2	0.0865	0.173	9.13	33.3	0.39
5	2 (700)	1	1	1	2	0.135	0.451	5.17	77.3	0.48
6	2	2	1	2	1	0.131	0.263	6.37	58.7	0.42
7	2	1	2	2	2	0.208	0.695	9.08	68.5	0.35
8	2	2	2	1	1	0.134	0.268	4.87	54.3	0.43
9	3 (900)	1	1	1	1	0.192	0.640	4.37	77.0	1.05
10	3	2	1	1	2	0.233	0.467	4.22	68.1	1.04
11	3	1	2	2	1	0.176	0.586	4.75	78.6	0.91
12	3	2	2	2	2	0.357	0.713	4.85	72.5	1.45

^a Other reaction conditions: $T = 100$ °C, $p = 1.1$ MPa, $y_{H_2}/y_{CO} = 48.3/51.7$, $C_{lig}/C_{cat} = 18$, $C_{cat} = 1.5 \times 10^{-3}$ kmol/m³, 2 h reaction time.

^b r_L was based on total liquid volume and r_O on the organic phase volume.

^c Observed values after 2 h reaction time.

^d Parameter values at different levels.

^e *n*-Decane was used as organic diluent for adjusting the concentration of 1-dodecene to 2.2 kmol/m³.

Table 3
Relative importance of various factors to each index of hydroformylation determined by margin analysis

Relative importance	Primary → secondary				
r_L					
Factor	N	C_d	C_{CTAB}	V_O/V_W	Stirrer
Level	900	4.4	12.3	1/1	PBTU
r_O					
Factor	N	V_O/V_W	C_d	Stirrer	C_{CTAB}
Level	900	3/7	4.4	PBTU	12.3
n/i					
Factor	N	V_O/V_W	Stirrer	C_d	C_{CTAB}
Level	500	3/7	PBTU	4.4	12.3
x					
Factor	N	V_O/V_W	Stirrer	C_d	C_{CTAB}
Level	900	3/7	DT	2.2	12.3
P					
Factor	N	Stirrer	C_d	V_O/V_W	C_{CTAB}
Level	500	PBTU	2.2	3/7	11.0

conversion and the minimum power consumption of agitation are given in Table 3. The most influential parameter was the intensity and mode of agitation, and the effect of surfactant concentration was less important, within the scope of selected reaction conditions. Variance analysis of experiments was also made to evaluate the influence of various factors and to reveal the significance of each variable to the indexes based on its corresponding value of the F -distribution function [34]. The results of variance analysis were similar to those of margin analysis, except for a different sequence of influence of two secondary factors, i.e. the concentrations of CTAB and 1-dodecene to the index of conversion.

Although the optimal set of variable levels corresponding to each index was not completely coincident, the optimal reaction conditions for compromise of high productivity and selectivity and low power consumption were found to be $N = 700$ rpm, $V_O/V_W = 3/7$, $C_d = 4.4$ kmol/m³, $C_{CTAB} = 12.3 \times 10^{-3}$ kmol/m³ and the stirrer type PBTU. The optimal value of the organic to aqueous phase volume ratio agrees with that obtained by Zhang et al. [21]. The reaction rate and regioselectivity were enhanced by a decrease of V_O/V_W , and this change of reaction performance is attributed to easy and stable formation

of micelles and O/W emulsion. As $C_d = 4.4$ kmol/m³ corresponded to pure 1-dodecene as the organic phase, this favored improved yield of linear aldehyde and avoided the need for additional separation of inert organic diluent. When the agitation speed was increased, power consumption, conversion and initial rate all increased, whereas the regioselectivity to n -tridecyclic aldehyde diminished. The orthogonal experimental results also showed that the concentration of surfactant and stirrer configuration had an important impact on the performance of the biphasic hydroformylation system. Hence, further studies in the extended range were conducted as follows, for the purpose of interpreting the reaction and improving operation of the process.

3.3. Influence of surfactant concentration

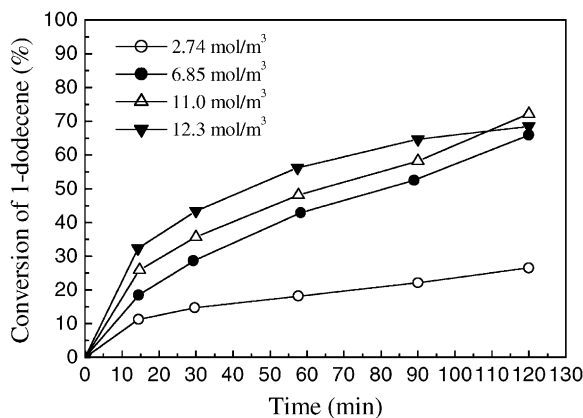
Fig. 3 and Table 4 illustrated the obvious influence of surfactant on the performance of biphasic hydroformylation of 1-dodecene remarkably, but there was no obvious effect on the power consumption of motor. The increase of CTAB concentration led to elevated initial reaction rate, conversion and normal/isomeric aldehyde ratio. In the beginning, when the CTAB concentration was changed from 2.74×10^{-3} to 6.85×10^{-3} kmol/m³, the initial rate, conversion and regioselectivity of 1-dodecene hydroformylation each increased rapidly. When the concentration of surfactant exceeded 6.85×10^{-3} kmol/m³, further increase of the molar ratio of normal/isomeric aldehyde and olefin conversion first were reduced, and then decreased slightly, whereas the initial rate still increased with elevated CTAB concentration. The results reported by Chen et al. [19] also give a similar trend for

Table 4
Influence of CTAB concentration on biphasic hydroformylation of 1-dodecene^a

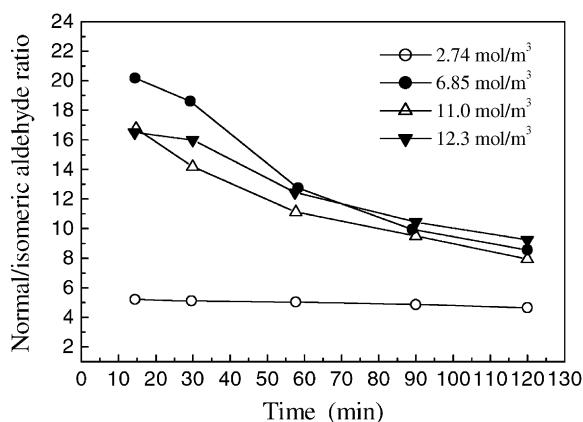
$C_{CTAB} \times 10^3$ (kmol/m ³)	$r_L \times 10^3$ (kmol/m ³ /s)	$r_O \times 10^3$ (kmol/m ³ /s)	n/i^b	x (%) ^b	P (W)
2.74	0.0325	0.108	4.65	26.3	0.31
6.85	0.0835	0.278	8.57	65.9	0.34
11.0	0.168	0.560	7.93	72.2	0.41
12.3	0.208	0.695	9.08	68.5	0.35

^a Reaction conditions are the same as in Fig. 3.

^b Observed values after 2 h reaction time.



(a) Conversion of 1-dodecene



(b) Normal/isomeric aldehyde ratio

Fig. 3. Influence of CTAB concentration on the biphasic hydroformylation of 1-dodecene. Reaction conditions: $N = 700$ rpm, $T = 100^\circ\text{C}$, $p = 1.1$ MPa, $V_O/V_W = 3/7$, $y_{\text{H}_2}/y_{\text{CO}} = 48.3/51.7$, $C_{\text{cat}} = 1.5 \times 10^{-3}$ kmol/m³, $C_d = 4.4$ kmol/m³ (60 ml 1-dodecene), $C_{\text{lig}}/C_{\text{cat}} = 18$, PBTU (stirrer): (a) conversion of 1-dodecene; (b) normal/isomeric aldehyde ratio.

the effect of CTAB concentration on conversion and selectivity in the presence of toluene as co-solvent.

When the concentration of cationic surfactant CTAB in a mixed organic–aqueous solution is kept sufficiently low, the surfactant remains as monomer at the interface of organic–aqueous phases. If the concentration is raised beyond the so-called critical micellar concentration (CMC), micelles are formed and spherical micelles may be turned into rod-like or lamellar micelles, or even form a microemulsion at

high concentration. The CMC of CTAB in a reaction mixture that mimics 1-dodecene hydroformylation was reported to be about 0.6×10^{-3} kmol/m³ at 90°C [19], therefore, it was believed that all runs in this work were carried out with the concentration of surfactant sufficiently high so that CMC and micelles were formed.

At elevated CTAB concentration, an increase of micelles with more orderly steric microstructure and interfacial area brought about further enrichment of rhodium catalyst in the interfacial layer, attracted by static electricity supposedly [19], which was beneficial for acceleration of the biphasic hydroformylation reaction and for formation of linear aldehyde. At sufficiently high CTAB concentrations, micelles may be induced to expand and even to form compact O/W microemulsion. Under these conditions the increase of total interfacial area was limited, which caused the observed phenomenon of slow increase of catalytic activity. However, a gradual increase of initial hydroformylation rate with increasing surfactant concentration was maintained, and this probably accounted for the slight extent of emulsification and lower quantity of aldehyde at the initial reaction stage. Emulsification of the reaction mixture became significant only after prolonged reaction time under mechanical agitation. As the reaction proceeded, more and more polar aldehydes formed in the biphasic mixture, which affected occurrence of static electricity in the mixture, and consequent harm to preservation of an orderly micelle microstructure. In fact, after 2 h at very high CTAB concentration the reaction mixture appeared to be a solid–liquid mixture. No significant separation was observed at ambient temperature, which indicated that the concentration of surfactant should be optimized further for commercialization.

3.4. Influence of agitation configuration

In order to make further optimization of reaction performance indexed by the chemical conversion and regioselectivity of the biphasic hydroformylation of 1-dodecene, it is necessary to explore an appropriate agitation configuration as well as the intensity of agitation, which affects the hydrodynamics of mixing and dispersion correlated with interphase mass transfer. A preliminary exploration on the suitable reactor configuration for 1-dodecene hydroformylation has been

performed [29]. In this paper new test data have been analyzed and compared with the previous results. Five cases of agitation configurations were tested. Cases 1 and 2 were standard surface aeration configurations using single DT and PBTU, respectively. Novel composite impeller configurations were featured with a SRFB located between the gas–liquid interface and the DT impeller (Case 3) or PBTU impeller (Case 4) to improve surface aeration. As shown in Fig. 1, dual impeller including an upper DT used as surface aerator and a PBTU fixed in the middle of reactor for circulating the reaction mixture was combined with a SRFB placed above the DT, and this composite agitation configuration was Case 5 [35].

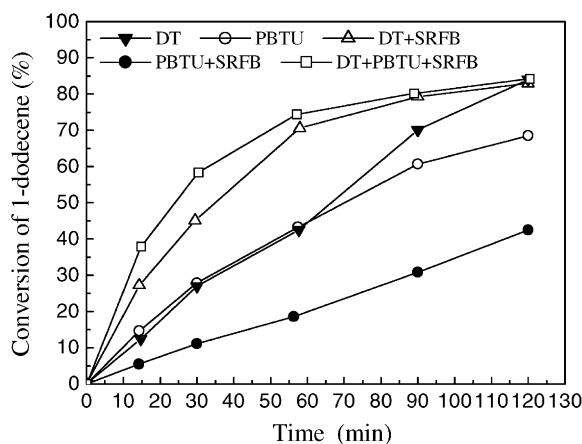
As shown in Fig. 4 and Table 5, the single PBTU impeller (Case 2) achieved better performance with higher initial rate and normal/isomeric aldehyde ratio accompanied with lower power consumption than the single DT impeller (Case 1) under the same operation conditions. This was possibly due to the better capability for overall circulation and lower agitation intensity of the PBTU impeller, which was in favor of maintaining the orderly micelle structure. When the novel baffle of SRFB was used (Cases 3 and 5), the initial rate of the biphasic hydroformylation increased remarkably from $0.630 \times 10^{-3} \text{ kmol/m}^3$ (Case 1) to 1.24×10^{-3} and $2.03 \times 10^{-3} \text{ kmol/m}^3$, almost by a factor of 2–3. However, the conversion and regioselectivity after 2 h reaction were almost the same. Therefore, it is clear that SRFB can increase the initial rate of 1-dodecene hydroformylation, but fails to further enhance the conversion and selectivity over a full 2 h run. The poor performance in Case 4 was probably caused by the failure of self-rotating and floating of the SRFB placed above the PBTU, with the consequence that normal contact, circulation and mixing of gas and liquid streams were weakened.

Table 5
Effect of agitation configuration on hydroformylation of 1-dodecene^a

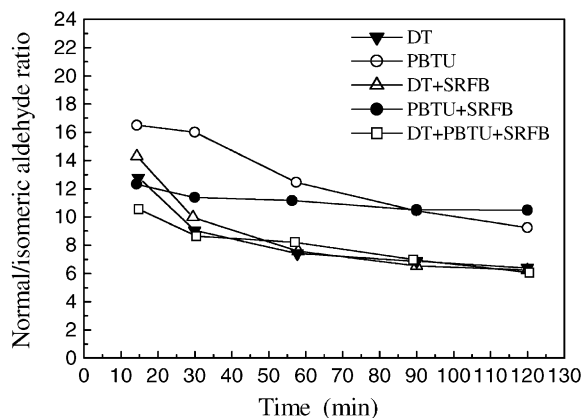
Case	Stirrer type	$r_L \times 10^3 \text{ (kmol/m}^3\text{/s)}$	$r_O \times 10^3 \text{ (kmol/m}^3\text{/s)}$	n/t^b	$x \text{ (%) }^b$	$P \text{ (W)}$
1	DT	0.189	0.630	6.39	84.0	0.42
2	PBTU	0.208	0.695	9.08	68.5	0.35
3	DT + SRFB	0.372	1.24	6.24	83.0	0.56
4	PBTU + SRFB	0.0620	0.207	10.5	42.8	0.41
5	DT + PBTU + SRFB	0.609	2.03	6.06	84.2	–

^a Reaction conditions are the same as in Fig. 4.

^b Observed values after 2 h reaction time.



(a) Conversion of 1-dodecene



(b) Normal/isomeric aldehyde ratio

Fig. 4. Hydroformylation conversion and regioselectivity versus reaction time with different agitation configuration. Reaction conditions: $N=700 \text{ rpm}$, $y_{H_2}/y_{CO}=48.3/51.7$, $T=100^\circ\text{C}$, $p=1.1 \text{ MPa}$, $V_O/V_W = 3/7$, $C_{\text{cat}} = 1.5 \times 10^{-3} \text{ kmol/m}^3$, $C_{\text{CTAB}} = 12.3 \times 10^{-3} \text{ kmol/m}^3$, $C_{\text{lig}}/C_{\text{cat}} = 18$, $C_d = 4.4 \text{ kmol/m}^3$ (60 ml 1-dodecene): (a) conversion of 1-dodecene; (b) normal/isomeric aldehyde ratio.

Yu et al. [33] demonstrated that the composite surface aeration configurations with SRFB were effective in enhancing the gas–liquid volumetric mass transfer coefficient by intensifying gas–liquid–liquid turbulence flow, generating more gas bubbles and obtaining smaller bubbles by stronger shear. Since the gas–liquid mass transfer of biphasic hydroformylation systems may be limiting [28], the composite agitation configuration shows better performance in promoting the reaction rate and is recommended for a stirred autoclave. According to the above results, it can be concluded that improving the agitation mode and operation intensity in gas–liquid and gas–liquid–liquid systems requires as much attention as the catalytic chemistry.

3.5. Emulsification of reaction mixture

As depicted in Figs. 2–4, the molar ratio of normal to isomeric aldehyde decreased significantly with time. This phenomenon, correlated with the mechanism of biphasic hydroformylation, requires careful interpretation for practical applications. Since the ease of phase separation by gravity for the collected liquid samples at different reaction times was quite different, it was necessary to investigate the relationship between regioselectivity and emulsification.

It is believed that the extent of emulsification is a reflection of operating conditions and physicochemical properties of the reaction system. Because it is very difficult to characterize quantitatively the emulsification extent, a simple but somewhat subjective and fuzzy index is thus proposed to represent the emulsification extent [29]. The defined fuzzy index ranges from 0 (significant phase settlement in less than 1 min after withdrawal from the reactor) to 5 (severe emulsification and resembles a solid with no phase separation by gravity observed over 4 h at ambient temperature), and for intermediate values, 1 is assigned to the situation with significant phase separation in 1–5 min, 2 for 5–20 min, 3 for 20–60 min and 4 for 1–4 h. Moreover, significant phase separation was observed for each sample after the mixture heated close to the reaction temperature of 100 °C.

As shown in Figs. 5 and 6, the extent of emulsification was observed to develop as the hydroformylation reaction proceeded, and to become gradually more severe with increase of agitation intensity and CTAB concentration. The agitation configuration

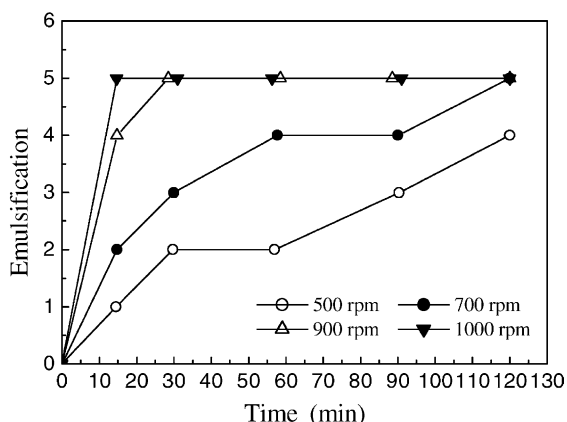


Fig. 5. Influence of agitation speed on emulsification. Reaction conditions are the same as in Fig. 2.

with higher olefin conversion produced more severe emulsification (Fig. 7). The emulsification became progressively more severe with reaction time, in a similar trend to conversion, and in a reversed trend to the ratio of normal/isomeric aldehyde (Figs. 2–4), and that, in general, less emulsification appeared to be beneficial to regioselectivity (Fig. 8). It may be conjectured that the oscillating microstructure of micelles accompanied with severe emulsification was not kept as orderly and compact as that in the beginning of reaction, and this effect not only increased difficulty of product separation at the end of reaction, but also was unfavorable for the formation of linear aldehyde. Otherwise, a probable reason might be that the iso-

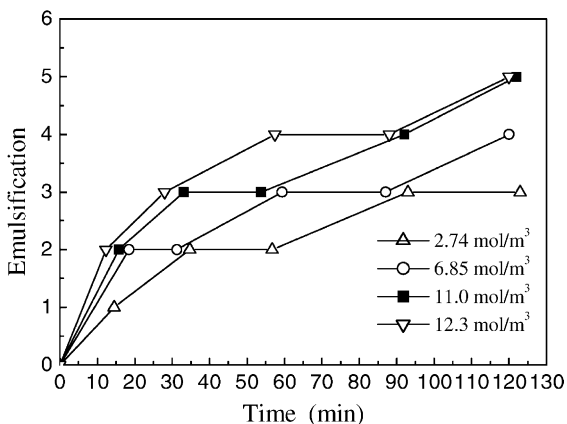


Fig. 6. Influence of surfactant concentration on emulsification. Reaction conditions are the same as in Fig. 3.

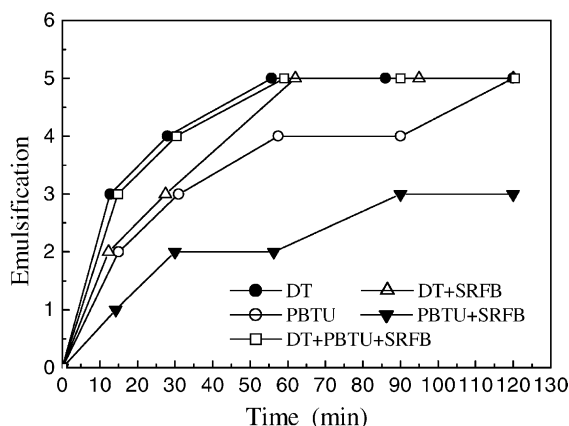


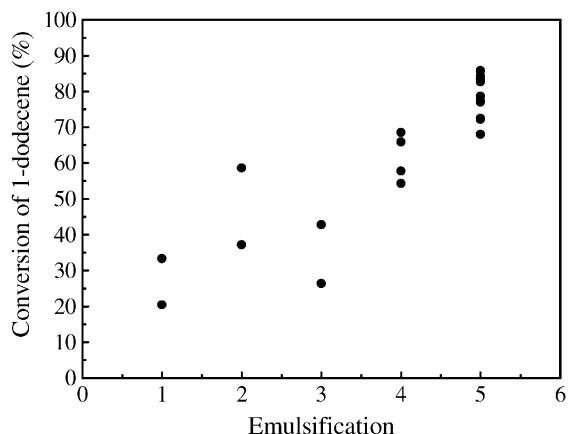
Fig. 7. Influence of agitation configuration on emulsification. Reaction conditions are the same as in Fig. 4.

merization of *n*-tridecylic aldehyde to isotridecylic aldehyde occurred as the hydroformylation reaction proceeded, but it is difficult to explain that the normal/isomeric aldehyde ratio, retained almost constant with time when the CTAB concentration was $2.74 \times 10^{-3} \text{ kmol/m}^3$ or the agitation speed was over 900 rpm.

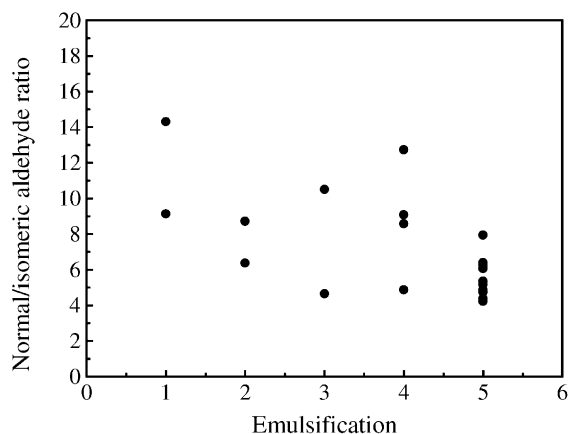
Since no clear and quantitative explanation is available at present for the complicated relationship between the reaction productivity and regioselectivity and the emulsification extent, more efforts are required to better understand the underlying intrinsic mechanism of biphasic hydroformylation and characterize emulsification more accurately by other physical indexes, such as droplet and bubble size, optical refraction, micelle microstructure etc.

3.6. Macro-kinetic models

Up to now no universally accepted intrinsic kinetic model has been derived for biphasic hydroformylation of olefins, on account of the incompletely clarified reaction mechanism and complicated effects of multiphase mass transfer. Summarizing results reported in literature, the kinetic rate of hydroformylation has been found to be influenced positively by increasing the concentration of catalyst, olefin and hydrogen, whereas increased carbon monoxide exerted a negative effect. The apparent activation energy required for aldehyde formation has been found to be in the range from 30 to 100 kJ/mol. The regioselectivity



(a) Conversion of 1-dodecene



(b) Normal/isomeric aldehyde ratio

Fig. 8. Hydroformylation conversion and regioselectivity versus emulsification extent of reaction mixture in 2 h under different reaction conditions based on the experimental data in Tables 1, 2, 4 and 5: (a) conversion of 1-dodecene; (b) normal/isomeric aldehyde ratio.

aspects have hardly been treated by kinetic analysis, and few reports on this problem have been published. Gholap et al. [36] detailed a kinetic selectivity study on hydroformylation of propylene using unmodified cobalt carbonyl catalyst under high-pressure conditions. Based on some conjecture about the mechanism of 1-dodecene hydroformylation, previous work [21,22] presented several more complicated kinetic models, including the influence of concentrations of higher olefin and catalyst, partial pressures of H_2

and CO, molar ratio of ligand to catalyst, volume ratio of organic/aqueous phase, weight percentage of surfactant and temperature. The macro-kinetic data including intrinsic chemical reaction and mass transfer under practical technological conditions provide the necessary basis for modeling and designing multiphase reactors. Reaction rate and regioselectivity models have been developed in an attempt to describe the macro-kinetics of biphasic hydroformylation of 1-dodecene in the presence of CTAB and thereby enable further quantitative analysis.

The following simple power rate equation was used to fit the aforementioned experimental data (18 in total) except for Cases 3, 4 and 5 with SRFB:

$$Y = A_0 N^{k_1} C_{\text{CTAB}}^{k_2} C_d^{k_3} \left(\frac{V_O}{V_W} \right)^{k_4} \quad (1)$$

where the dependent variable Y represented the initial rate (r_L) or the ratio of normal/isomeric aldehyde (n/i). The four independent variables considered refer to mass transfer of biphasic system combined with intrinsic kinetics, since the agitation factor was not previously incorporated [21,22]. The logarithm of the above equation was adopted for multiple linear regression. The objective was to minimize the least square of error between predicted and experimental logarithmic variables as defined by

$$\phi = \sum_{i=1}^N (\ln Y_{\text{cal},i} - \ln Y_{\text{exp},i})^2 \quad (2)$$

The corresponding optimized values of kinetic model parameters are listed in Table 6. The initial reaction rates of r_L were found to agree with an average relative deviation of 14.8% and the observed n/i ratios under different reaction conditions were within 12.0% average deviation when compared with the experimental data.

The estimated parameters of empirical macro-kinetic expressions indicated clearly that high initial rate and regioselectivity were achieved with increase in

olefin and CTAB concentrations, and that high agitation speed or organic/aqueous phase volume ratio increased the initial reaction rate but inhibited linear aldehyde formation. If the variable N of agitation speed in Eq. (1) was replaced by the power consumption (P), the corresponding average relative deviation between the predicted and the experimental results became 25.4% for r_L and 13.8% for n/i . The increased deviation was caused by the experimental error in measuring power consumption.

4. Conclusions

Biphasic hydroformylation of 1-dodecene catalyzed by water-soluble rhodium catalyst $\text{RhCl}(\text{CO})(\text{TPPTS})_2$ was investigated using a 500 ml autoclave, especially the effects of reaction engineering factors detailed. High agitation intensity was beneficial for olefin conversion and reaction rate, but adversely affected the normal/isomeric aldehyde ratio. Some novel agitation configurations have been shown to be effective in promoting interphase mass transfer rate in the gas–liquid–liquid hydroformylation system, thus increasing the initial rate and improving the n/i ratio of products. Increase of surfactant concentration led to elevated initial reaction rate, conversion and normal/isomeric aldehyde ratio, especially at low CTAB concentration. The extent of emulsification had a remarkably positive effect on conversion and a negative effect on regioselectivity of hydroformylation system, and consequently on the separation of the aqueous catalyst phase from the organic phase. Macro-kinetic models have been developed for the initial reaction rate and the ratio of normal/isomeric aldehyde. This work indicates that further systematic chemical engineering study combined with thorough understanding of the interfacial catalytic mechanism is required for reliable scale-up of gas–liquid–liquid reactors with high productivity and energy efficiency for the hydroformylation of 1-dodecene and other long chain olefins.

Table 6
Values of model parameters of two kinetic equations

Index	A_0	k_1	k_2	k_3	k_4
r_L (kmol/m ³ /s)	9.66×10^{-11}	2.79	1.11	0.792	0.177
n/i	2.64×10^2	-1.47	0.281	0.156	-0.264

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