Preliminary Exploration of the Reactor Configuration for Hydroformylation of 1-Dodecene Catalyzed by Water Soluble Rhodium Complex*

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Abstract Hydroformylation of 1-dodecene was studied in a biphasic system using water-soluble rhodium complex [RhCl(CO)(TPPTS)$_2$] as catalyst in the presence of cetyl trimethyl ammonium bromide as surfactant to enhance the reaction rate. Efforts were devoted to improve the performance of hydroformylation by exploring reactor configuration which enhanced the mixing, dispersion and interphase mass transfer. Experiments were carried out in a 0.5 L autoclave at the total pressure of 1.1 MPa and temperature from 363 K to 373 K. Several surface aeration configurations were tested, and higher hydroformylation rate with higher normal/branched aldehyde ratio produced were achieved. The experiences suggest that improved reactor configuration by taking reaction engineering measures is beneficial to better process economy in alkene hydroformylation.

Keywords 1-dodecene, biphasic hydroformylation, gas-liquid-liquid reactor, reaction engineering, surface aeration, emulsification, n/i ratio

1 INTRODUCTION

Hydroformylation of olefins is an important commercial process for production of aldehydes and alcohols. Homogeneous catalysis is gradually giving the way to heterogeneous catalysis for easy separation and recovery of catalyst from the mixture of reaction products and solvent. The biphasic (aqueous-organic) hydroformylation of propylene has been successfully commercialized to produce butyraldehyde using water soluble rhodium complexes as catalyst[1,2]. When it is applied to the hydroformylation of higher olefins, the reaction rate becomes very low for actual insolubility of higher olefins in the aqueous phase[3−6]. However, the addition of cosolvent or surfactant can enhance the reaction rate[3−8].

The biphasic hydroformylation of higher olefins occurs in a typical gas-liquid-liquid system. The nature of new catalytic complexes and ligands will certainly determine the intrinsic activity and selectivity of such catalysts. However, an equally important factor is the effectiveness of contact of gas and liquid reactants with the catalyst contained in certain phase. It largely depends on the hydrodynamics of gas-liquid-liquid dispersion, interphase mass transfer, solubility and phase equilibrium, interfacial properties, as well as the intrinsic kinetics of concerned reactions. Hence, research and development work on high performance heterogeneous reactor is of great significance to

the commercialization of biphasic hydroformylation of higher olefins.

Chen *et al.* have investigated the biphasic hydroformylation of 1-dodecene using RhCl(CO)(TPPTS)$_2$/TPPTS as catalyst in the presence of surfactant cetyl trimethyl ammonium bromide (CTAB)[5,9]. The ratio of normal to branched aldehyde in the reaction product is rather high (up to 6). The reaction rate was also significantly enhanced by the surfactant. It is found that many engineering factors such as agitator type, agitation speed, reactor configuration *etc.* present great influence on the reaction conversion and the ratio of normal/isomeric aldehyde in the product from biphasic hydroformylation[8,10,11].

The central topic of research and development work on hydroformylation of higher olefins toward commercialization is the chemical reactor for complex catalysis in multiphase systems. The usual type of reactor used for hydroformylation is the stirred autoclave, but it should be adapted to the catalyst used for hydroformylation with specific chemical engineering features. Commercial reactors for hydroformylation was generally equipped with agitator, device for gas distribution and dispersion, and heat exchanger, so as to achieve effective mixing, reasonable gas holdup and good temperature control. The typical reactor for biphasic hydroformylation of propylene was patented

by Ruhrchemie[12], in which the stirrer drives the reacting gas-liquid-liquid dispersion upwards in the draft tube. In the top space the unreacted gas is separated from the dispersion and fed back to the reactor by an external compressor. The liquid-liquid dispersion flows downwards in the annulus and circulates up again in the draft tube. In the expanded settling zone in the upper section of the reactor, part of the light oil phase is separated from the dispersion by gravity and is withdrawn at a controlled rate.

Since the hydroformylation demands long residence time for reaction, no technical measure is effective in rendering the gas residence time long enough while keeping sufficient gas-liquid contact area. In such a situation, gas reactant has to be fed in excess and the gas recycling is revoked for reaction economics. The current authors think that surface aeration is an attractive measure to reduce excessive gas feed and eliminate the gas circulating system. In this paper, we report the preliminary efforts of searching for the better configuration of surface aeration multiphase reactor for 1-dodecene hydroformylation in a biphasic catalytic system, and the exploring experience in improving agitation in the reactor is thought beneficial to the development of a novel industrial hydroformylation reactor.

2 EXPERIMENTAL

Hydroformylation of 1-dodecene was carried out in a similar way as in the previous experiments[8] in a stirred stainless steel autoclave with a capacity of 0.5 L with a 65 mm ID. This reactor was equipped with an automatic temperature control system consisting of an external electrical heating jacket and an internal cooling coil. The temperature can be maintained within ± 1 K and the pressure within ± 5 kPa. The reactor is agitated with a Rushton turbine stirrer.

The complex catalyst $RhCl(CO)(TPPTS)_2$ and water-soluble ligand [TPPTS: $P(m\text{-}C_6H_4SO_3Na)_3$] were provided by Sichuan University, Chengdu, China. 1-Dodecene was purchased from Fluka, Switzerland and Aldrich Co., USA. Syngas (mixture of CO and H_2) was procured from Beijing Huayuan Chemical Gas Co., China. CTAB was of analytical purity. Deionized water was used in all experiments. The syngas were purified by passing through dehydration, decarbonylation, desulfurization and deoxidation columns before charged into the reactor.

In a typical experimental run, the required amounts of catalyst, ligand and surfactant were added and dissolved in the reactor, then the organic phase of 1-dodecene was added to make the total volume of 200 ml. The reactor was flushed with nitrogen first,

and then with syngas, then heated to the specified temperature. After that, the syngas was introduced at the desired pressure and kept constant during the whole run. Hydroformylation reaction was started by switching on the stirrer. Liquid samples (< 2 ml each) were collected at regular intervals and analyzed by a gas chromatography.

3 RESULTS AND DISCUSSION

It is well known that the mixing and dispersion of phases are critical to multiphase reaction. In particular for optimization of the hydroformylation reactor performance indexed by the chemical conversion and the ratio of normal to isomeric aldehyde products, it is necessary to explore the suitable selection of agitating stirrer type and better combinations. In this work, several efforts were attempted to contribute to the optimal reactor configuration.

3.1 Dual impeller configuration

As compared with the standard configuration with a 36 mm diameter 6 blade disk turbine (DT) (Fig. 1), the dual Rushton impeller (Fig. 2) and the dual composite impeller (Fig. 3) were tested. The previous study showed that under the recommended operation conditions, the gas-liquid mass transfer resistance was not reduced to a negligible level in some cases[8]. It is desired to take some engineering measures to enhance the rate of mass transfer of gas reactants into the liquid phases. Increasing the agitation speed is effective in promoting the gas-liquid mass transfer, but it is found that excessively strong agitation intensifies the emulsification extent and lead to difficulty of separation of two liquid phases after reaction as discussed in section 3.3. This in turn decreases the overall rate of hydroformylation while increasing the power consumption. It is therefore preferred to explore further the reactor configuration, impeller type and impeller combination for enhancing the interphase mass transfer effectively.

Study on the agitation in gas-liquid-liquid systems indicates that using dual or composite impeller would improve the overall mixing in the stirred tank and increase the volumetric gas-liquid mass transfer coefficient[13]. In this work, a dual Rushton impeller (Fig. 2) and a dual composite impeller (Fig. 3) were tested. In these two cases, surface aeration configuration is adopted, which is believed to be more energy-efficient because the gas reactants can be entrained into the liquid phase dispersion as bubbles and the recovery, recompression and recycle of unreacted gas are avoided. In Fig. 2 the upper Rushton disk turbine is used as the surface aerating stirrer and placed close to the gas-liquid surface. A second stirrer fixed onto
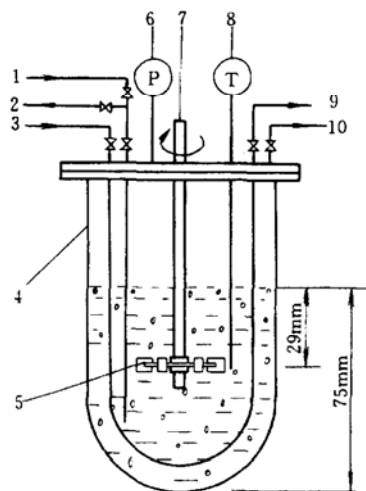
Figure 1   Hydroformylation autoclave with a
standard Rushton stirrer
1—gas inlet; 2—sampling port; 3—cooling water inlet;
4—autoclave; 5—Rushton turbine; 6—pressure gauge;
7—agitation shaft; 8—thermocouple;
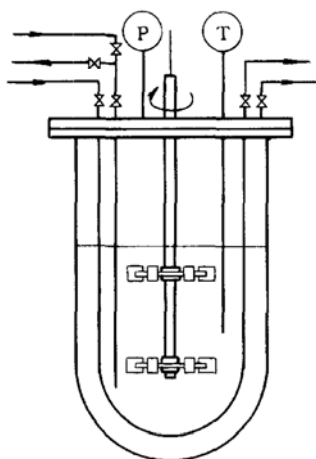9—cooling water outlet; 10—gas vent

Figure 2   Dual Rushton impeller equipped autoclave
(The upper and lower Rushton disk turbines are 15 mm and
45 mm below the liquid surface respectively)

the same shaft in the middle of the reactor distributes the entrained bubbles throughout the autoclave by the liquid stream discharged from the stirrer. In the configuration depicted in Fig. 3, the circulating stirrer is a pitched blade turbine upward (PBTU), which pumps the dispersion upwards. There is a report on the combination of different stirrers that when combined with a surface aeration a pitched blade turbine upward is more efficient than a pitched blade turbine downward as the gas-liquid mass transfer is concerned[14].

Under the same operation conditions as reported in the previous work ($n = 15\,\mathrm{r\cdot s^{-1}}$, $p = 1.1\,\mathrm{MPa}$, $y_{H_2}/y_{CO} = 53/47$, $T = 363\,\mathrm{K}$, $c_{cat} = 1.0\,\mathrm{mol\cdot m^{-3}}$, $[P]/[Rh] = 18$, $w_{CTAB} = 0.3\%$, $V_L = 0.2\,\mathrm{L}$, organic
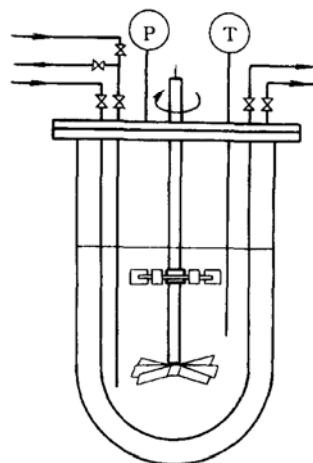

Figure 3   Dual composite impeller equipped
autoclave
(The upper Rushton disk turbine and the lower pitched blade
impeller are 15 mm and 45 mm below the liquid surface
respectively)

phase: 1-dodecene, $V_O/V_W = 1/1$)[8], hydroformylation of 1-dodecene was conducted in configurations 2 and 3 so that the reactor performance can be compared with the results reported previously using the standard configuration (Fig. 1). Fig. 4(a) shows the contrast of results of hydroformylation in 2 h, demonstrating that the superiority of the composite stirrer: it gave the higher conversion of 1-dodecene, 59.6%, whereas the standard configuration achieves 42.0% only. The higher conversion can be attributed to enhanced gas-liquid and liquid-liquid mass transfer. The dual Rushton impeller gave the conversion of 45.8%, only marginally higher than the single Rushton disk turbine, probably the overall mixing in the reactor is not improved much due to the poor efficiency of the combination of two identical Rushton turbines. Fig. 4(b) shows the (n/i) ratio is inversely correlated with the conversion, and the improved agitation by the composite impeller seems detrimental to the formation of normal aldehyde. If the comparison is made by the initial reaction rate for three configurations shown in Fig. 4, the initial rate of hydroformylation, r_0, of the composite impeller is the highest with the value of 0.0336 kmol·m^{-3}·min^{-1}, 0.0230 kmol·m^{-3}·min^{-1} is for the dual Rushton turbine, and the lowest is 0.0166 kmol·m^{-3}·min^{-1} for the standard Rushton configuration.

Figure 5 gives the results under $n = 10\,\mathrm{r\cdot s^{-1}}$ and otherwise the same reaction conditions. It also demonstrates clearly the superiority of the composite stirrer (the conversion of 45.5% in 2 h) over the standard Rushton impeller (conversion of 31.8%). The (n/i) ratio at $n = 10\,\mathrm{r\cdot s^{-1}}$ is rather high as compared with that in Fig. 4 with higher agitation speed at $n=15\,\mathrm{s^{-1}}$,
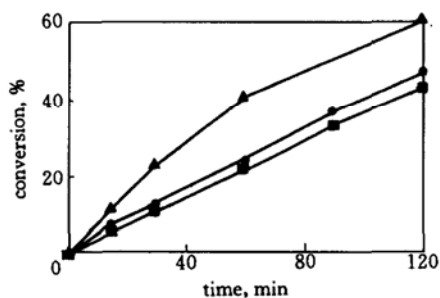
(a) Conversion

(b) (n/i) ratio
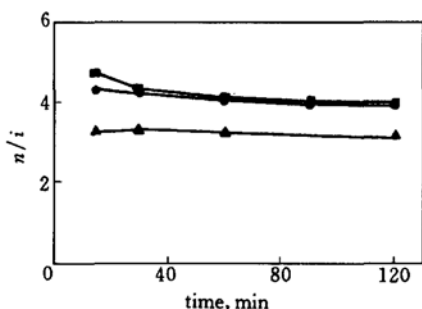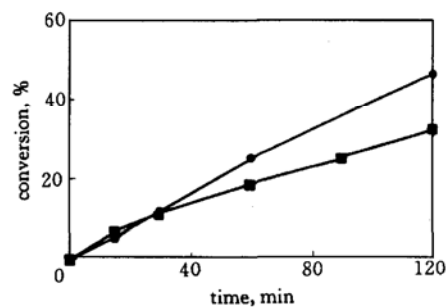
Figure 4 Hydroformylation conversion versus
agitation configuration at $n = 15\,r\cdot s^{-1}$
($p = 1.1\,MPa$, $y_{H_2}/y_{CO} = 53/47$, $T = 363\,K$,
$c_{cat} = 1.0\,mol\cdot m^{-3}$,
[P]/[Rh] = 18, $w_{CTAB} = 0.3\%$, $V_L = 0.2\,L$, organic phase:
1-dodecene, $V_O/V_W = 1/1$)
—■— standard Rushton; —●— dual Rushton; —▲—
composite impeller

(a) Conversion

(b) (n/i) ratio

Figure 5 Hydroformylation conversion versus
agitation configuration at $n = 10\,r\cdot s^{-1}$
($p = 1.1\,MPa$, $y_{H_2}/y_{CO} = 53/47$, $T = 363\,K$,
$c_{cat} = 1.0\,mol\cdot m^{-3}$,
[P]/[Rh] = 18, $w_{CTAB} = 0.3\%$, $V_L = 0.2\,L$, organic phase:
1-dodecene, $V_O/V_W = 1/1$)
—■— standard Rushton; —●— composite impeller

and again the composite impeller gives lower value
of (n/i) in correspondence to strong agitation by the
composite impeller. However, it is noticed that the
time courses in the conversion between the standard
configuration and the composite stirrer are different
for two agitation speeds. The difference may come
from the different emulsification of the reaction mix-
ture: at $n = 10\,r\cdot s^{-1}$, emulsification is less serious and
the phase separation in samples for gas chromatogra-
phy is faster, while $n = 15\,r\cdot s^{-1}$ makes the separation
of organic and aqueous phases more difficult.

3.2 Agitation configuration with self-rotating floating baffle (SRFB)

Many chemical engineering measures can be taken
to improve the liquid dispersion, mixing and the over-
all interphase mass transfer rates. Mao et al. proposed
a composite surface aeration configuration[15], whose
effectiveness in enhancing the gas-liquid mass trans-
fer rate in a stirred vessel was demonstrated by Yu
et al.[16]. This configuration is adopted here for hy-
droformylation of 1-dodecne and is depicted in Fig. 6.
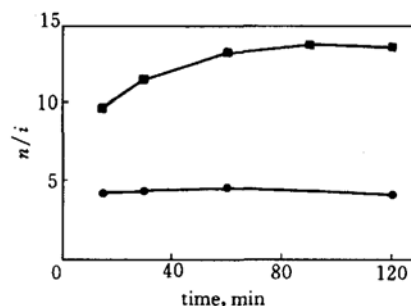The self-rotating floating baffle (SRFB) is 35 mm in

diameter, made from a circular stainless steel sheet
with thickness of 0.14 mm. A central hole is made for
fitting itself onto the shaft so as to rotate and float
freely around the shaft. The sheet is radially cut to
the $\phi13$ mm circle to form 12 fan blades. Every blade
is twisted by 30° angle to the horizontal plane to en-
sure the baffle afloat over the DT when impinged by
the swirling stream discharged from the disk turbine.

The 1-dodecene hydroformylation experiment was
conducted under the conditions of $n = 11.7\,r\cdot s^{-1}$, to-
tal $p = 1.1\,MPa$, $y_{H_2}/y_{CO} = 52/48$, $T = 373\,K$,
$c_{cat} = 1.5\,mol\cdot m^{-3}$, [P]/[Rh]=18, $w_{CTAB} = 0.45\%$,
$V_L = 0.2\,L$, undiluted 1-dodecene, $V_O/V_W = 3/7$. The
control run was conducted with the standard Rushton
impeller under the same experimental conditions. As
shown in Fig. 7, the initial hydroformylation rate r_0 is
increased from 0.0378 to 0.0743 $kmol\cdot m^{-3}\cdot min^{-1}$, al-
most by a factor of 2. However, the conversions at
2 h of reaction time are almost the same (84.0% for
the control, 83.0% for the SRFB+Rushton impeller).
In contrast to the results in Fig. 4, the initial rate of
0.0166 $kmol\cdot m^{-3}\cdot min^{-1}$ for the standard Rushton im-
peller is obtained at $n = 15\,r\cdot s^{-1}$, the current rate of
0.0743 $kmol\cdot m^{-3}\cdot min^{-1}$ is at $n = 11.7\,r\cdot s^{-1}$. It can be
concluded that the high initial rate is achieved with

much lower power consumption, since the agitation power is proportional to the 5 th power of n under the comparable conditions. An obvious observation is the SRFB apparently increases the initial rate of hydroformylation but fails to improve the conversion at the end of a 2 h experimental run. A single pitched blade turbine upward with 36 mm diameter behaves similarly as the Rushton impeller.
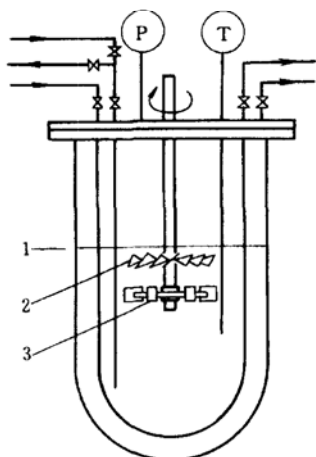

Figure 6   Surface aeration configuration with a Rushton impeller combined with a SRFB
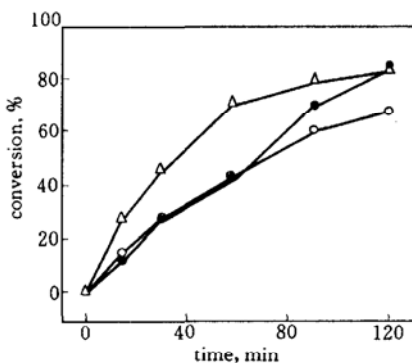[The baffle (2) is 8mm below the liquid surface (1) and lower Rushton turbine (3) 35mm below (1)]

Figure 7   The effect of SRFB on conversion of 1-dodecene
($n = 11.7\,\mathrm{r\cdot s^{-1}}$, $p = 1.1\,\mathrm{MPa}$, $y_{H_2}/y_{CO} = 52/48$, $T = 373\,\mathrm{K}$,
$c_{cat} = 1.5\,\mathrm{mol\cdot m^{-3}}$, [P]/[Rh]=18, $w_{CTAB} = 0.45\%$, $V_L = 0.2\,\mathrm{L}$,
organic phase: 1-dodecene, $V_O/V_W = 3/7$)
—O— PBTU; —●— standard Rushton;
—△— SRFB+Rushton

As indicated in Fig. 8, the SRFB+Rushton impeller leads to similar (n/i) as that by the standard Rushton impeller, and on the contrary the single PBTU impeller gives much higher values of (n/i), probably due to its better capacity of circulation and lower intensity of agitation. It is noticed that the ratio of (n/i) decreases significantly as the hydroformylation proceeds, in a similar trend as the progressively

serious emulsification if it is represented by a fuzzy index addressed in section 3.3. These phenomena need careful examination and interpretation.
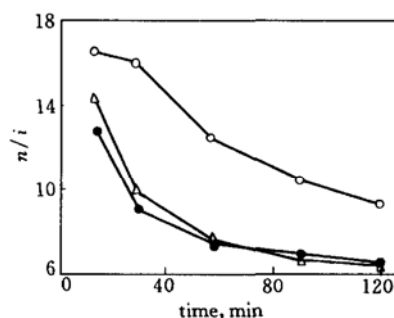

Figure 8   The effect of SRFB on (n/i) of 1-dodecene hyfroformylation at $n = 11.7\,\mathrm{r\cdot s^{-1}}$
($p = 1.1\,\mathrm{MPa}$, $y_{H_2}/y_{CO} = 52/48$, $T = 373\,\mathrm{K}$,
$c_{cat} = 1.5\,\mathrm{mol\cdot m^{-3}}$, [P]/[Rh]=18, $W_{CTAB} = 0.45\%$,
$V_L = 0.2\,\mathrm{L}$, organic phase: 1-dodecene, $V_O/V_W = 3/7$)
—O— PBTU; —●— standard Rushton;
—△— SRFB+Rushton

3.3 Fuzzy observation of emulsification

From the gravity separation of phases in the samples for analysis collected at different reaction times, it is observed that the easiness of phase separation is quite different. The time taken for phase separation ranges from several minutes to tens of hours, obviously related to the extent of emulsification. It is recognized that the emulsification extent is the reflection of operating conditions and the physicochemical properties of the hydroformylation system. It was considered beneficial to record the severity of emulsification for further data analysis. Thus, a simple but somewhat subjective and fuzzy index was suggested to represent the extent of system emulsification, which ranges from 0 (significant phase settlement in less than 1 min. in a 2 ml ampoule) to 5 (severe emulsification and no phase separation by gravity observed over 4 h). For intermediate extent, 1 was assigned to the situation with phase separation in 1—5 min, 2 for 5—20 min, 3 for 20—60 min, and 4 for 1—4 h. The emulsification extent may be characterized more accurately by many physical indexes, such as average droplet size, optical refraction etc. in addition to the phase separation time. In this work, the intention is only tentative demonstration of the relationship between the hydroformylation indexes (the conversion and n/i ratio) and the emulsification extent by using such a fuzzy index.

In Fig. 9, the emulsification is observed to develop as the hydroformylation proceeds. However, the difference in the emulsification extent is present only in the first half hour between the standard and SRFB+Rushton impellers, and less emulsification seems beneficial to the reaction rate of hydroformyla-

tion in Fig. 7 and higher (n/i) value in Fig. 8. Figs. 8 and 9 also demonstrate the parallelism of the emulsification extent to the value of (n/i) ratio and the fact that hydroformylation in a less emulsified mixture gives rise to more normal aldehyde. This is also the case for the experiment of hydroformylation with a 6-blade PBTU under the same conditions.
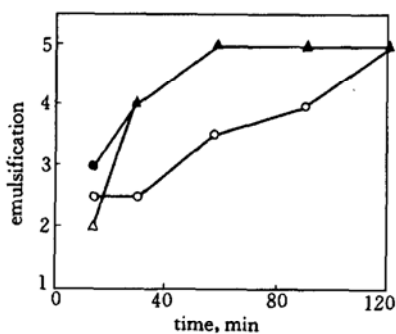

Figure 9   Emulsification *versus* agitation configuration at $n = 11.7\,\mathrm{r\cdot s}^{-1}$
($p = 1.1\,\mathrm{MPa}$, $y_{H_2}/y_{CO} = 52/48$, $T = 373\,\mathrm{K}$, $c_{cat} = 1.5\,\mathrm{mol\cdot m}^{-3}$, [P]/[Rh]=18, $w_{CTAB} = 0.45\%$, $V_L = 0.2\,\mathrm{L}$, organic phase: 1-dodecene, $V_O/V_W = 3/7$)
—○— PBTU; —●— standard Rushton;
—△— SRFB+Rushton

At present no clear and quantitative explanation is available for the complicated relationship among the reaction rate, the (n/i) ratio and the extent of emulsification, and more efforts are required to better understand the underlying mechanisms. However, since definite microstructure is formed in the reacting emulsion and is related to the surfactant CTAB used for promoting hydroformylation rate[10], it may be conjectured that the formation of micelles at the first period of reaction when agitation is started is critical to r_0 and (n/i) ratio of the entire process of hydroformylation, and the initial features of these micelles such as size, shape, kennel content *etc.* might prevail in the whole hydroformylation. Otherwise, it is hardly conceivable that emulsions formed by Standard Rushton and SRFB+Rushton configurations (with different dispersing ability) lead to different hydroformylation rates but almost the same (n/i) ratio. Why the emulsions formed by Rushton (with high shear rate) and PBTU (with low shear) lead to almost the same time course of hydroformylation but quite different (n/i) ratio? The microemulsion structure features (initial formation and evolution during hydroformylation) may possibly provide the answers.

Based on the above experience in hydroformylation and the general study on the chemical engineering properties of gas-liquid and gas-liquid-liquid systems, improved reactor configurations for bench-scale hydroformylation can be proposed tentatively in the next stage of research. As demonstrated in the above, variations in agitation mode and operation lead to remarkable change in the performance and efficiency of 1-dodecene hydroformylation in the surface aeration dead-end reactors. For reliable scale-up of a gas-liquid-liquid reactor with high reaction and energy efficiency, further systematic chemical engineering study combined with thorough understanding of the interfacial hydroformylation mechanism is urgently desired.

4   CONCLUSIONS

(1) Improvement of the performance of biphasic hydroformylation of 1-dodecene catalyzed by water soluble catalyst $RhCl(CO)(TPPTS)_2$ in the presence of cationic surfactant CTAB by different agitation/aeration configurations is investigated in a 0.5 L autoclave. Some configurations are confirmed to be effective in promoting mixing and enhancing gas-liquid mass transfer, and thus increasing the initial hydroformylation rate and improving the product (n/i) ratio in a stirred tank with a gas-liquid-liquid hydroformylation system. This suggests the great potential of chemical engineering measures in the optimization of the process development toward commercial production of high aldehydes by biphasic hydroformylation.

(2) It is observed that high agitation intensity is beneficial to high conversion of olefin, but is disadvantageous for high aldehyde (n/i) ratio. Certain compromise between conversion and (n/i) ratio can be achieved by compromised operation in suitable agitation configuration.

(3) The extent of emulsification of the reacting dispersion mixture shows obvious relevance to the hydroformylation rate and the product (n/i) ratio, in addition to its direct effect on the post-reaction separation of the catalyst from the organic phase containing olefin and aldehyde. The complicated interrelation of emulsification to the process performance demands further investigation of the emulsion microstructure and the interfacial reaction mechanism when cationic surfactant added in the system.

(4) Based on the experience on different reactor configurations, a reactor configuration with an effective composite impeller for surface aeration, phase dispersion and overall mixing seems suitable for hydroformylation of high olefins on a larger scale.

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NOMENCLATURE

c	concentration, $kmol \cdot m^{-3}$
n	stirrer speed, $r \cdot s^{-1}$
[P]/[Rh]	ligand/catalyst molar ratio
p	total pressure, MPa
r_0	initial reaction rate per organic phase volume, $kmol \cdot m^{-3} \cdot min^{-1}$
(n/i)	normal/isomeric ratio
V	liquid volume, L
V_O/V_W	organic/aqueous volume ratio
w_{CTAB}	mass percentage of CTAB in water, %

Subscripts

cat	catalyst
CO	carbon monoxide
CTAB	cetyl trimetyl ammonium bromide
G	gas phase
H_2	hydrogen
L	liquid
O	organic phase
T	total
W	aqueous phase

REFERENCES

1 Kuntz, E. G., "Homogeneous catalysis in water", *CHEMTECH*, **17**, 570—575 (1987).

2 Wiebus, E., Cornils, B., "Water-soluble catalysts improve hydroformylation of olefins", *Hydrocarbon Processing*, **66**, 63—64 (1996).

3 Wu, J. Ch., Yuan, G., Zhou, Q. Zh., "The preparation of higher aldehydes by using water-soluble rhodium-phosphine complex catalysts", *Petrochemical Industry*, **20**, 79—85 (1991). (in Chinese)

4 Bahrmann, H., Lappe, P., "Process for the preparation of aldehydes by hydroformylation using rhodium-phosphine catalysts and phosphonium salt solubilizers", EP 602463, (1994).

5 Chen, H., Liu, H. C., Li, Y. Z., Cheng, P. M., Li, X. J., "The study of hydroformylation of higher olefins catalyzed by water-soluble rhodium-phosphine complex — the effect of reaction conditions", *Journal of Molecular Catalysis (China)*, **9**, 145—151 (1995). (in Chinese).

6 Purwanto, P., Delmas, H., "Gas-liquid-liquid reaction engineering: hydroformylation of 1-octene using a water-soluble rhodium complex catalyst", *Catal. Today*, **24**, 135—140 (1995).

7 Laura, T., Edoardo, P., "Process and catalysts for the hydroformylation of olefin in microemulsions", EP 380154 (1990).

8 Zhang, Y. Q., "Macro-kinetics and reactor configuration of biphasic hydroformylation of 1-dodecene", Ph. D. Thesis, Institute of Chemical and Metallurgy, Chinese Academy of Sciences Beijing (1999). (in Chinese)

9 Chen, H., Li, Y. Zh., Cheng, P. M., Yang, Q., Li, X. J., "The study of hydroformylation of 1-dodecene catalyzed by water soluble rhodium-phosphine complex at atmospheric pressure", *Journal of Molecular Catalysis (China)*, **8**, 347—352 (1994). (in Chinese)

10 Chen, H., Li, Y. Z., Cheng, P. M., He, Y., Li, X. J., "Micellar effect in high olefin hydroformylation catalyzed by water-soluble rhodium complex", *J. Mol. Catal. A: Chem.*, **149**, 1—6 (1999).

11 Bi, X. Y., Yang, C., Mao, Z.-S., "Effect of reaction engineering factors on kinetics and normal/isomeric aldehyde ratio of hydroformylation of 1-dodecene", *J. Chem. Ind. Eng. (China)*, **52** (7), 570—572 (2001). (in Chinese)

12 Cornils, B., Hibbel, J., Konkol, W., Lieder, B., Much, J., Schmidt, V., Wiebus, E., "Verfahren zur Herstellung von Aldehyden", EP 103810 (1984).

13 Yu, G. Z., "Chemical engineering characteristics of gas-liquid-liquid system", Ph. D. Thesis, Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing, China (2001). (in Chinese)

14 Patwardhan, A. W., Joshi, J. B., "Hydrodynamics of a stirred vessel equipped with a gas-inducing impeller", *Ind. Eng. Chem. Res.*, **36** (9), 3904—3914 (1997).

15 Mao, Z.-S., Yu, G. Z., Wang, R., "A composite surface aerator", *Chinese Patent Application*, 00102745.X, Feb. 22, (2000). (in Chinese).

16 Yu, G. Z., Mao, Z. S., Wang, R., "A novel surface aeration configuration for improving gas-liquid mass transfer", *Chinese J. Chem. Eng.*, **10** (1) 39—44 (2002).