Mixing Problems for High Viscosity Fluids in polymer Production Processes

*Y. Murakami · *K. Fujimoto · *T. Shimada · *M. Sekino · *K. Asano · *A. Yamade and *T. Tou

*Dept. of Chem. Eng., Kyushu Univ., Fukuoka, Japan

Abstract

There have been a few studies on high viscosity mixing devices. However, there exists no universally accepted technique for evaluating their functional status in the light of generalized basic information such as the flow patterns, shearing and tensile deformation characteristics in the mixing equipment. The first part of this paper gives a physical meaning to the mixing number $C_r=\nu T_\nu$ and the shearing amount, $C_s=T_\nu \sqrt{\nu \varepsilon_d / \mu}$ by using a simplified Mohr's striation thickness theory. The second part of this paper, the degree of surface renewal action is studied by comparing the value estimated from the flow patterns on a free surface of a liquid with that from a gas absorption characteristics. The third part of this paper gives a review for heat transfer problems some considerations on discrepancies between different investigators in heat transfer problems Newtonian and non-Newtonian fluids.

Introduction

Before entering the items, reactors and processes for high viscosity fluids are summarized as the following.

High viscosity liquids are used in polymer synthesis, food industries etc., the former of which is the most typical where the simultaneous chemical reactions are accompanied. Practical techniques have been secret since they are the fundamental process for manufacturing the newly developed polymers. Details are being revealed in patents and literatures published recently. However, they are not much enough to comprehend individual processes of polymerization in its whole aspects. The followings are to be noted before taking up the main subject.

(1) Viscosity considered ranges 50~5000 poises which is expected to be standard.

(2) Several examples of reactors discussed involve the new types to be noted as well as the conventional ones. Applied processes are also mentioned partly to help further comprehension.

It would be important that process engineers of polymerization take a wide view of selection of polymerizers. It is recommended to decide the fundamental combination and function first and then examine details of individual equipments.

Table 1 shows the estimated percentage of reactors in employment in Japan with respect to the reactor geometry. The values are based on the amount of
Table 2. Processes of mass Polycondensation polymerization

<table>
<thead>
<tr>
<th>Final React</th>
<th>By Product</th>
<th>TmPC</th>
<th>(K)</th>
<th>Process</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH] + HCOOH</td>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH] + HCOOH</td>
<td>260~270</td>
<td>4~5</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH]</td>
<td>HCOOH</td>
<td>260~270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH]</td>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH] + HCOOH</td>
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<td>H_2N[CH_2CH_2OCOCH_2CH_2OH]</td>
<td>HCOOH</td>
<td>260~270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2N[CH_2CH_2OCOCH_2CH_2OH]</td>
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<td></td>
<td></td>
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<td>HCOOH</td>
<td>260~270</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Stirred Tank Tower Special polymer industry (total) (wt%) 90 10 2
(Plastic, Synthetic fibre Rubber) 70 30 7
Synthetic fibre industry more frequently production, i.e. Generally speaking, stirred tanks are used but tower types are sometimes used in synthetic fibres production processes. Special types probably include continuous processes of polyurethane and polyester groups. Combined types are very often used in polymerizing systems from two main considerations. The first is related to the problem of heat removal and the reaction conversion. In vinyl-type polymerization reactions, violent heat generation occurs at the initial stage, thus requiring a perfectly mixed reactor at the sacrifice of the conversion. The conversion increases gradually as exponential function at the final stage and therefore a pistonflow reactor is preferred to obtain the higher conversion.

The other is the fact that a step of prepolymerization is necessary depending of mechanisms and characteristics of polymerization (polyester, nylon 66 etc.) as shown in Table 2. Referring to the reactor itself, it is important to remove condensates in polycondensation polymerization reactions. It is necessary to reduce the film thickness or to promote the renewal rate of free surface for the rapid removal of these rate-controlling by-products in case of batch and continuous systems.

Stirred tank reactors are most frequently used as mentioned before. Details of geometry, heat transfer and mechanical structure of stirred tanks used in the emulsion and the suspension polymerizations have been discussed very often in the available literatures and therefore they are not mentioned here. The shorter time cycle with batch systems has been aimed at and heating systems, impellers and discharge vents have been improved. However, there have been a few studies on high-viscosity mixing devices. However, there exists no universally accepted technique for evaluating their functional status in
the light of generalized basic information such as the flow patterns and shearing and tensile deformation characteristics in the mixing equipment. This paper deals with the measurement of flow patterns and power consumption in several types of mixers used in a high viscosity range, which include an anchor, a paddle, a double helical ribbon, a multistage double pitched paddle (MIG), a helicone (single & double) mixer, an apparatus with two agitator axes having multidisks (Du pont type) and motionless mixer such as a Kenics type static mixer.

After obtaining the overall flow patterns in a mixer, circulation capacity and fluid deformations which cover an information as to the energy dissipation in an agitated field are correlated with the homogenizing time. The viscosity covered by the empirical correlations for heat transfer coefficients on a vessel wall is about 500 poises at highest and mostly less than scores of poises. Anchors, large paddles, herical ribbons mixer and the combinations of them with scrapers are frequently used as agitating impellers. Special types such as kneader are sometimes employed but data on heat transfer properties are few available. An consistent interpretation of the experimental results has been given yet throughout both Newtonian and non-Newtonian fluid media and much discrepancies still remains between different investigators.

1. Flow Patterns

1.1 Experimental Apparatus and Procedures

Impellers and vessels used for the measurement of flow patterns were made of acrylic resin and the geometrical configuration is shown in Fig. 1. The cylindrical vessel was enclosed with a squaresided acrylic vessel filled with the same fluid in order to reduce optical distortion.

The velocity was determined by taking photographs of tracer polystyrene spheres which were illuminated with a slit ray of a mercury lamp. Fig. 2 shows the camera angle and the direction of slit ray, in which the slit widths were 3 mm and 5 mm for horizontal sections and vertical sections, respectively. For horizontal sections, the camera and the impeller were synchronously rotated in order to observe the
stream lines simultaneously. The slit widths were determined by considering the fluid velocity through the slit width and shutter speed of camera. The average diameter and density of tracer polystyrene spheres used were 0.047 cm and 1.04 g/cm³ respectively. The terminal velocity of tracers was about 0.00022 cm/sec in this experiment, which was about 0.015% of blade tip velocity and about 0.30% of average axial velocity \( v_2 \). The aqueous solutions of corn syrup were used as highly viscous materials. Velocity data were obtained by means of measuring tracer loci on the double enlarged photographs with slide callipers.

1.2 Resulting Flow Patterns

Figs. 3 and 4 show the examples of tracer loci. Figs. 3, 4, 5, 6, 7, 8, 9 and 10 show the representative flow patterns for eight types of mixers.

**Anchor (AN)** The tangential flow is dominant and becomes small as going away from the impeller. The axial flow does not exist except in a bottom region at such a low Reynolds number. The radial flow is fairly recognized near the impeller, but it should be noted that the essential exchanges in a radial direction hardly exist because of a creeping flow as shown in Fig. 3.

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Large Paddle (PA) The axial flow does not exist like the anchor. On the whole the shear action is strong, but the flow is a circulation flow. Therefore the fluid elements are considerably sheared, but the exchange of fluid elements in either hemicylinder in either side of paddle is of no existence. (Fig. 4)

Helical ribbon (HR) The tangential flow is almost the same as in the case of the anchor. The axial flow is remarkably recognized and it forms an assumed complex flow tube which has a elliptical section along the blade. The fluid elements are circulated in this flow tube, where the shear action is poor in the inside of tube and strong in the outside. They are given a high shear action and there exists a strong exchange of fluid elements. The radial flow is not so large. (Fig. 5)

Mixing apparatus with two agitator axes having multidisks (DU) This apparatus has a wide free surface and the region of free surface rotates almost like a solid body. The shear action suffers between disks. In this region of free surface, although the quantitative measurement could not be done, the axial flow is recognized according the visual observation of tip tracer. Therefore, this region is good enough for axial circulation and delivers to the shear region between disks. However, this axial flow is not so large. (Fig. 6)

Single helicone (S-HC) This type of impeller shows the flow pattern similar to that of HR as shown in Fig. 7. The performance of circulation in the vessel deteriorates remarkably by the existency of shaft.

Double helicone (D-HC) The axial flow accompanied with the circulation around the blade are remarkably observed as shown in Fig. 8. On the whole the liquid is sheared significantly and the exchange of fluid in each cone vessel is remarkably recognized.

MIG The installation of baffles is possible in this mixing system. The change of flow pattern by installing baffles is shown in Fig. 9. Flow pattern is almost similar to that HR.

Motionless mixer (ML) Fig. 10-(a) given the axial flow pattern in a device equipped with assembled motionless mixer units as shown in Fig. 1-(h). The flow reversal due to the highly developed flow is caused by these units. The plug flow condition is
approached as shown in Fig. 11. A displacement characteristics of fluid element is obtained as shown in Fig. 10-(b).

1.3 Distributions of dissipation energy
From the flow pattern, the distribution of dissipation energy was obtained by the following formula.

\[
P_{vg}/\mu = 2\left[\left(\frac{\partial \psi_r}{\partial r}\right)^2 + \frac{1}{r} \left(\frac{\partial \psi_r}{\partial \theta} + \psi_r\right)^2 \left(\frac{\partial \psi_r}{\partial \phi}\right)^2\right] + \frac{1}{H} \left(\frac{\partial \psi_r}{\partial \phi} + \frac{1}{r} \frac{\partial \psi_r}{\partial \theta}\right)^2 + \left(\frac{\partial \psi_r}{\partial r} + \frac{\partial \psi_r}{\partial \phi}\right)^2 \right]
\]

(1)

Fig. 12 shows the distributions in a given horizontal section. It becomes clear that the high shear region is maldistributed near the blade. Consequently, for high viscosity apparatus it is a problem how the fluid moves into and out of high shear region.

In Eq. (1), underlined terms A, P and H are dominant (>80~90%) for an anchor, a paddle and a helical ribbon, respectively.

2. An Evaluation of Circulation, Capacity of High Viscosity Mixing Devices

Flow pattern is a very important factor to move fluid readily into every part of the vessel. The relation \(nT_M = C_1\) might be connected with axial circulation flow rate. The relation between the circulation capacity given by the flow pattern and a constant \(C_1\) are summarised in Table 3, which are well correlated as \(nT_M = 3N_c\) by considering an axial flow rate only. An axial circulation capacity may also be considered as an efficiency which exhibits whether the supplied power is used effectively in mixing processes.

<table>
<thead>
<tr>
<th>Impeller</th>
<th>(N_q)</th>
<th>(N_q)</th>
<th>(N_c)</th>
<th>(3N_c)</th>
<th>(nT_M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anchor</td>
<td>0.37</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ribbon</td>
<td>0.37</td>
<td>0.081</td>
<td>11</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>Screw with</td>
<td>—</td>
<td>0.42</td>
<td>14</td>
<td>42</td>
<td>45</td>
</tr>
<tr>
<td>draft tube</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. A Process of Homogenizing by Shear Action in High Viscosity Mixing Devices
In this section, the shear rate obtained from the flow pattern is correlated with a homogenizing time in high viscosity mixer. The following discussions are based on a concept of striation thickness by Mohr. The physical meaning of the judge of a final state of the homogenization by conventional methods seems not to be evident.

Efficiency of homogenizing process proposed by Shimada is also introduced in this section. A method of estimation of scale up constant, $C_2$ proposed by Fujimoto is also discussed.

3.1 Development

Applying the theory of Mohr's striation thickness to a uniform shear field, the following formula is derived.

$$\frac{L_0}{L_M} = M = MT_M (M > 1) \quad (2)$$

where $L_0$ and $L_M$ are the scale of fluidic element at the original and the final state of mixing, respectively.

A tangential annular flow between two coaxial cylinders is taken as an uniform shear field model. If the ratio $\kappa$ of the inner diameter to the outer one is assumed as $\kappa \approx 1$, the shear rate becomes $M = 2\pi k\kappa / (1 - k)$. Therefore Eq. (2) gives the following relation for mixing time.

$$nT_M = (L_0 / L_M) \left[ (1 - \kappa) / 2\pi \kappa \right] \quad (3)$$

On the other hand, the power consumption is shown as follows.

$$\sqrt{P_{vgc}/\mu} = 4\pi k\kappa / (1 - \kappa^2) \quad (4)$$

From Eqs. (3) and (4),

$$T_M \sqrt{P_{vgc}/\mu} = [2/(1 + \kappa)] \left( L_0 / L_M \right) \quad (5)$$

The above relation seems to explain a physical meaning of $T_M \sqrt{P_{vgc}/\mu} = \text{const.}$, that is, the term $2/(1 + \kappa)$ may be a constant depending on a geometrical configuration of an apparatus and the term $L_0 / L_M$ may be a constant depending on the essential scale of fluid elements at the final state of mixing. The former term is complex for generally used mixers. It is for the case of $\kappa = 1$ that the stage of homogenizing process could be thought to be ideal. The ideal limit of $T_M \sqrt{P_{vgc}/\mu}$ may be equal the scale ratio $L_0 / L_M$.

Now in widely used high-viscosity mixing devices which have a good circulation, the following relations have been generally concluded in laminar flow system as shown in Table 4.

$$nT_M = C_1 \quad (\text{const.}) \quad (6)$$

$$T_M \sqrt{P_{vgc}/\mu} = C_2 \quad (\text{const.}) \quad (7)$$

<table>
<thead>
<tr>
<th>Types of mixers</th>
<th>C</th>
<th>C1</th>
<th>C2</th>
<th>([\text{Re}] \sqrt{P_{vgc}/\mu} )</th>
<th>([nT_M] \sqrt{T_M \sqrt{P_{vgc}/\mu}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helical ribbon</td>
<td>300</td>
<td>18.1</td>
<td>33</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>(Nagata)</td>
<td>413</td>
<td>19.6</td>
<td>25.3</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Helical ribbon</td>
<td>200</td>
<td>8.4</td>
<td>45</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>(Gray)</td>
<td>416</td>
<td>4.1</td>
<td>220</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Helical screw</td>
<td>330</td>
<td>19.0</td>
<td>33</td>
<td>625</td>
<td></td>
</tr>
<tr>
<td>(Nagata)</td>
<td>260</td>
<td>23.3</td>
<td>25</td>
<td>581</td>
<td></td>
</tr>
<tr>
<td>S-SC (up-flow)</td>
<td>350</td>
<td>27.0</td>
<td>25</td>
<td>675</td>
<td></td>
</tr>
<tr>
<td>D-SC (down flow)</td>
<td>690</td>
<td>24.7</td>
<td>29.5</td>
<td>506</td>
<td></td>
</tr>
<tr>
<td>ML (type A)</td>
<td>--</td>
<td>8.4</td>
<td>44</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>ML (type B)</td>
<td>--</td>
<td>8.6</td>
<td>34</td>
<td>290</td>
<td></td>
</tr>
</tbody>
</table>

As seen from the above-mentioned discussions, the scaling up under the condition of Eq. (6) is considered to be that under a constant scale ratio. The observed scale $L_M$ is determined dependently of the mixing time judge system. Therefore, it should be emphasized that the relation of Eq. (6) or (7) does not provide the condition of the scaling up measure based on the absolute scale of fluid elements, but on the scale ratio.

In case of extending the above discussions generally used mixers, it will be required for the content of the term $\sqrt{P_{vgc}/\mu}$ that the shear action is dominant in mixing devices. The authors considered
a helical ribbon mixer as a generally used mixer, in which the shear action is seemed to be fairly dominant (80%) from the analysis of Eq. (1). Two types of amount of shear in a helical ribbon mixer are derived. One is the product $M_p$ of $T_M$ by $\sqrt{P_{tr}t^2/\mu}$ from power consumption, and the other is the product $M_f$ of $T_M$ by $\dot{M}$ from the flow pattern as follows.

\[ M_p = 19.3 \pi T_M \quad (8) \]
\[ M_f = N_C (M_1 t_1 + M_2 t_2) \quad (9) \]
\[ T_M = N_C (t_3 + t_4) \quad (10) \]

where \( t_1 = t_2 \), \( M_1 = 18.6 \pi \), \( M_2 = 4.0 \pi \)

\[ M_f = 11.3 \pi T_M \quad (11) \]

The latter is the mean amount of shear considering the flow rate as follows.

\[ M_s = \int_0^1 \dot{M}_s v_s \, ds/\int_0^1 v_s \, ds \quad (12) \]

where subscripts, 1 and 2, represent respectively two regions in case of deviding the flow field into a high-shear region and a low-shear one in a helical ribbon mixer.

### 3.2 Experiment

The mixing experiments are examined in a cone rotor type mixer as a uniform shear field model and a helical ribbon mixer as a representative of general high-viscosity mixers. The cone rotor mixer is shown in Fig. 13 and the measurement of mixing time is carried out by a method of reaction of $1\% \text{Na}_2\text{S}_2\text{O}_3$, in which a minor component is $1\%$ corn syrup solution, 15.5 g $\text{I}_2$/kg corn syrup solution, and a major component is $\text{Na}_2\text{S}_2\text{O}_3$-corn syrup solution, 15.4 g $\text{Na}_2\text{S}_2\text{O}_3$-5$\text{H}_2\text{O}$/kg corn syrup solution. The shear rate in a cone rotor mixer and the average shear rate in a helical ribbon mixer derived from power consumption are nearly identical, which are 2.4 sec$^{-1}$ and 2.57 sec$^{-1}$ respectively, because a chemical reaction is used as a judge of the final state of mixing.

### 3.3 Results and discussion

The scale $I_M$ at a judge of the final state of mixing for a cone rotor mixer is determined as $L_M = 0.0018 \text{cm}$ although the judge is fairly delicate. The results for a helical ribbon are summarized in Fig. 13 and Tab. 5, which show that the discussion no Eq. (5) is probably available for the system having a dominancy of shear action. Two types of values of scale $L_M$ are calculated by using two types of shear rates stated previously.

### Table 5. Milling time and striation thickness for helical ribbon mixer

<table>
<thead>
<tr>
<th>$L_0$ [cm]</th>
<th>$T_M$ [sec]</th>
<th>$L_M$ [cm]</th>
<th>$L_M$ [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>230</td>
<td>1.18x10$^{-3}$</td>
<td>2.02x10$^{-3}$</td>
</tr>
<tr>
<td>1.00</td>
<td>236</td>
<td>1.65</td>
<td>2.81</td>
</tr>
<tr>
<td>1.00</td>
<td>200</td>
<td>1.96</td>
<td>3.32</td>
</tr>
<tr>
<td>1.23</td>
<td>225</td>
<td>2.08</td>
<td>3.63</td>
</tr>
<tr>
<td>1.23</td>
<td>268</td>
<td>1.79</td>
<td>3.05</td>
</tr>
<tr>
<td>1.40</td>
<td>245</td>
<td>2.22</td>
<td>3.79</td>
</tr>
<tr>
<td>1.57</td>
<td>290</td>
<td>2.11</td>
<td>3.59</td>
</tr>
<tr>
<td>1.70</td>
<td>290</td>
<td>2.54</td>
<td>4.34</td>
</tr>
<tr>
<td>2.00</td>
<td>317</td>
<td>2.45</td>
<td>4.19</td>
</tr>
</tbody>
</table>

| av. 2.00x10$^{-3}$ | 3.42x10$^{-3}$ |

There becomes $L_M = 0.0020 \text{cm}$ by Eq. (8) and $L_M = 0.0034 \text{cm}$ by Eq. (11). On comparing two values, the scale $L_M$ from the power consumption has a fairly good agreement with the scale $L_M$ of a
3.4 Shear Characteristics of High Viscosity Mixing Devices

The following method seems to give a useful measure of evaluating the shear characteristics in the mixer. The object of this method is an evaluation of some high-viscosity mixers and some flow fields without considering the difference of geometrical configurations of mixing devices. This method is suggested by kajimoto of Mitsubishi Heavy Industries Ltd., and the authors take \( \sqrt{P_{vgc}/\mu} \) or \( D \sqrt{P_{vgc}/\mu} / \alpha \) as a measure of dimensionless shear rate, which is obtained from the equation of correlation to power consumption. It has another variable indicating the close clearance between rotator or moving part and fixed wall, which is the ratio \( \varepsilon \) of the impeller diameter to the vessel one for generally used agitator systems of the inner diameter to the outer one for cylindrical annulus, the ratio \( C/D \) of the representative clearance to the vessel diameter for an apparatus having any clearance, or the ratio \( l/D_d \) of the distance between disks to the disk diameter for an apparatus with two agitator axes having multidisks. These ratios can be considered to be one criterion of shear field.

Fig. 14 shows these relations for some typical mixing devices and flow systems. This figure gives some practical techniques for evaluating the state of averaged shear characteristics for the apparatus.

Information as to mixing time is not included in the abovementioned method. The method of \( C_1 \) vs. \( C_2 \) plots shown in Fig. 15, which is proposed by shimada-kajimoto, gives information as to mixing time and power consumption for various kinds of mixing equipment used in the range of laminar region.

![Fig. 15 Mixing characteristics](image)

\( C_1 = nT_M 10^{3} \)

CB-Curved blade, CRT-Curved rod & turbine, EB-Elliptic blade, ER-Elliptic ribbon, IBP-Inclined blade paddle, PR-Propeller, SC-Screw, TU-Turbine,

(-S)-with screen, (-D)-with draft tube, (-B)-with baffle, (-O)-off centered

4. Homogenizing Characteristics of Kenics Type Motionless Mixer

Brunemann studied for some kinds of static mixers. The authors studied to obtain a common measure to have a comparison between motion type and motionless type mixer.

Homogenizing processes in the kenics type motionless mixer are shown in Fig.16.
For motionless mixer, $P_{vge}$ is calculated as follows.

$$P_{vge} = 2.0 \pi \alpha / D$$  (13)

when $f$ is the friction factor, the following relationship is obtained as to Type A and B shown in Fig. 1-6(h).

$$f = 2.25 (16/Re)$$  (14)

Experimental results are summarized in Table 4. The value of $C_4$ for double helical ribbon mixer is about two times that for kenics type motionless mixer. This relation tells that a limiting value of $C_4$ is about $C_1$ limit = 16 ($\approx 33/2$, $C_1$ = 33 is for helical ribbon).

5. Surface Renewal Action of Mixing Apparatus with Two Agitator Axes Having Multidisks (DU)

5.1 Experimental Procedures and results

If the surface renewal model of Danckwerts is applied for the batch operation, the rate of absorption is expressed as

$$N' = V a \sqrt{D v S} (C_a - C_d) \exp \left( -a \sqrt{D v S} t \right)$$  (15)

From Eq. (15) the capacity coefficient is determined by plotting $N'$ vs. $t$ and the experimental result is as follows.

$$K_L a = a \sqrt{D v S} = 0.58 a^{-1/2} v^{-1/2}$$  (16)

The surface area in this experiment was determined from the measurement of surface profile.

$$a = 2.62 \times 10^4 \ n^{-1/8} v^{-1}$$  (17)

From these relations the rate of surface renewal $S$ [cm$^3$/cm$^2$sec] is given as follows.

$$S_{obs} = 4.12 \times 10^{-4} n V$$  (18)

where the diffusivity of CO$_2$ in Glycerine was estimated from the extrapolated data of Calderbank$^{16}$ and our experimental data by the method of stagnant liquid surface ($Dv = 2.0 \times 10^{-7}$ cm$^2$/sec at 10.5 poises in viscosity and 20°C).

The authors assume that the rate of surface renewal can be estimated by the following formula.

$$S_{est} = 2 \nu L / A$$  (19)

Where $V_{m}$ [cm/sec] is the average rate of surface renewal, which was determined by the photographic measurement with the use of stroboscope.

$$V_{m} = 4.2 \nu$$  (20)

Accordingly, the rate of surface renewal can be estimated from Eqs. (17), (19) and (20) and the apparatus condition $L = 9.5$ cm as,

$$S_{est} = 3.95 \times 10^{-4} n^{1/6} V$$  (21)

Eq. (18) is fairly good agreement with Eq. (21).

5.2 Application to polycondensation polymerization reaction

As stated in the introduction, one of the primary purposes of this study is to make a recommendation of application of this apparatus to a bulk polycondensation reaction. There are miscellaneous liquid state polycondensations, such as nylon 66, 610, polyethylene terephthalate, polyurea and polycarbonate. An equilibrium exists in these reaction systems,
there then can be the following two reaction rate
determining steps according to the order of the value
of the equilibrium constants and permitted limit of
the boundary layer thickness of the diffusion of byproduct;

1. Polycondensation reaction
2. Diffusion of byproduct molecules in the liquid
state.

For example, the order of a permitted limit of
diffusion thickness, \( \delta c \), for nylon 66 have no trouble
in considering as about \( \delta c = 10^{-4} \sim 10^{6} \text{cm} \). When the
order of a boundary layer thickness is estimated by
\( 2 \sqrt{2D/t} \) (a cut point to determine the thickness is
taken about 95 \% of a byproduct concentration in
a liquid), a required degree of surface renewal
action, \( S \), for nylon 66 is calculated in the following
manner by assuming \( D_{V} \sim 10^{-8} \text{cm}^{2}/\text{sec} \) for the order of
diffusivity coefficient for byproduct.

\[
S = t^{-1} - 2D_{V}\delta c^{-2} = 8 \times 10^{-5} \times 1 \times 0.1^{-2} \sim 8 \times 10^{-5} \times 0.1^{-2} = 8 \times 10^{-5} \sim 8 \times 10^{-9} \text{sec}^{-1}
\]

The order of the degree of surface renewal action
in this experimental apparatus is larger than \( S = 10^{-1} \)
sec\(^{-1} \), which shows the rate determining step for
nylon 66 is polycondensation reaction characteristics
alone. On the contrary, polyethylene terephthalate
polycondensation has very small value of equilibrium
constant, about \( 10^{-5} \times \) (equilibrium constant for nylon
66), so that a driving force of the diffusion is also
reduced to the same order. The diffusion thickness
in the case of polyethylene terephthalate polyconden-
sation reaction has to be \( 10^{-5} \times \) (the order of liquid
thickness of diffusion for nylon 66), then,

\[
S = [2D_{V}\delta c^{-2}] \times 66 \times 10^{-4} = 0.8 \sim 80 \text{ sec}^{-1},
\]

which value gives a suggestion that a rate determining state.
From above mentioned discussions, engineering
considerations for nylon 66 are restricted to the
problem concerning with completion of the reaction.

6. Some Aspects of Heat Transfer in
Agitated Vessels Working with High
Viscosity Liquids

(An Evaluation of Estimating Method of Heat
Transfer Coefficients between Vessel wall and High
Viscosity Liquids)

6.1 Current tendency of heat transfer study
in agitated vessel

Ackley\(^{(b)}\) (1960) reviewed those investigations up to
1959. Chapman\(^{(d)}\) (1965) gave a review of literature
up to 1963, which is concerned with low viscosity
Newtonian fluids. Ito\(^{(e)}\) (1963) discussed non-Newtonian
heat transfer and gave useful recommendations.
“Mixing” edited by Uhl\(^{(a)}\) et al. summerizes many
works with the Newtonian liquid system up to 1962
and also deals with some aspects of the high viscosity
liquid system. A review by Penney\(^{(b)}\) et al. should
be referred to where the coloseclutter agitator in
the high viscosity liquid system is discussed. In
case of low viscosity liquids, the focus of
investigation has shifted from “average” heat transfer
to “local” behaviour since 1963. In connection with
this, some interesting researches have been published
on the inter-relation between momentum-, heat-and
mass-transfer phenomena in agitated vessels. In case of
high viscosity liquids, the investigation still remains
in a step of a view point of “average” behaviour
and in addition there exist some troubles in
estimating the average heat transfer coefficient.
Especially in many cases of non-Newtonian fluids the
proposed apparent viscosity does not have the clear
physical meaning.

6.2 Heat transfer studies with anchor agitators
6.2.1 In case of Newtonian fluids

Zlokarnik\(^{(d)}\) correlated his results for the high
viscosity system \( (\nu = 10^{-2} \sim 5 \times 10^{7} \text{ St}) \) in a different
from the conventional ones, which covers a rather
wide range of the operation variables corresponding
to \( Re = 1 \sim 10^{8} \) and includes the results of scraper
type. His proposed equation is

\[
Nu = a (Re Pr^{\frac{1}{3}} + b)^{\frac{2}{3}} (\nu b/\nu L)^{m}
\]

(22)

where values of \( a, b \) and \( m \) are shown in Fig. 17
and the bulk liquid temperature was estimated from
the heat balance. Fig. 18 shows a comparison with
the experimental results. A similar equation is given
by Mizushima and Murakami\(^{(e)}\) as follows
\( \text{Nu} = 0.4 \, \text{Re}^{0.75} \rho^{0.125} (\mu b / \mu w)^{0.14} \) for \( \text{Re} > 300 \) \hfill (23)

Zlokarnik employed the unsteady state technique while Mizushima, Murakami, the steady state one. A numerical comparison as shown in Fig. 19 shows a substantial agreement between calculated values using Eq. (22) and experimental values from which Eq. (23) was established. Re*, which is mentioned later, for non-Newtonian liquid case. The results by Uhl are the same as Eq. (23) with 0.4 replaced by 0.38, which was found, however, to vary with the ratio of d/D. Uhl\textsuperscript{(12)} pointed out the significance of the flow pattern and eddies formed in the vicinity of the agitator in the batch operation of anchor agitator with high viscosity liquid as schematically visualized in Fig. 20. He recommended the anchor agitator for Re > 300 where the following equation can apply

\[
\frac{k \mu D}{\lambda} = K \text{Re}^{1/2} \rho^{3/4} (\mu b / \mu w)^{0.12} \hfill (24)
\]

where

\[
\frac{1}{2} \left(1 - \frac{d}{D}\right) \quad 0.01 \quad 0.02 \quad 0.03 \quad 0.04 \quad 0.06
\]

\[
K \quad 0.38 \quad 0.38 \quad 0.38 \quad 0.42 \quad 0.47
\]

He explained the increase in \( k \) with the clearance

\[ J. \text{KIChE, Vol. 10, No. 6, Dec. 1972} \]
due to the effect of disturbance formed near the agitator. Mizushima and Murakami obtained the value of 0.4~0.6 for \( k \) when

\[
\frac{1}{2} \left( 1 - \frac{d}{D} \right) = 0.017 \text{ and } Re < 10^4
\]

The equation by Mizushima et al. is recommended for the scraper system. In case of Newtonian fluids the anchor is recommended for \( 300 > Re > 20 \) as well as for higher \( Re \) and Eq. (25) is applicable instead of Eq. (24). A little different value of

\[ K' = 1.05 \text{ at } \frac{1}{2} \left( 1 - \frac{d}{D} \right) = 0.076 \]

is given by Mizushima and Murakami. In case of pseudoplastic non-Newtonian fluid, the helical ribbon with scraper blades are recommended where \( h_j \) is taken as 90\% of that given by Eq. (27). When \( Re < 20 \), Eq. (26) proposed by Coyle et al. can be used where the rate controlling step is the heat conduction through half of clearance between the wall and the agitator tip.

\[
\begin{align*}
\frac{h_j D}{\lambda} &= K' Re^{1/2} Pr^{1/2} \left( \frac{m_p}{m_w} \right)^{0.14} \\
\frac{h_j D}{\lambda} &= 4 \left( 1 - d/D \right) \\
1/2 \left( 1 - d/D \right) &\quad 0.01 \quad 0.02 \quad 0.03 \quad 0.04 \quad 0.07
\end{align*}
\]

\[
K' \quad 1.2 \quad 0.9 \quad 0.9 \quad 1.0 \quad 1.3
\]

Mizushima et al. proposed Eq. (27) for the case of the anchor with scrapers while Eq. (25) reduces to Eq. (28) for the same geometry as that used by Mizushima et al.\(^{[12]}\)

\[
\left( \frac{Nu}{Pr} \right) = 2 \sqrt{\frac{Re}{Pr}} Re^{1/2} Pr^{1/2} \quad \text{Mizushima, } n_p = 2 \quad (27)
\]

\[
\left( \frac{Nu}{Pr} \right) = 0.934 (RePr)^{1/2} + 400 \quad \text{Zlokarnik} \quad (28)
\]

in which the constant, 400, is in turn negligibly small relative to the practical values of \( RePr \) greater than 10\(^4\). This simplification yields

\[
\left( \frac{Nu}{Pr} \right) = 1.71 \left( \frac{Pr}{Re} \right)^{1/2}
\]

indicating that the ratio of \( \left( \frac{Nu}{Pr} \right) \) is around unity for \( Pr = 500 \) and \( RePr = 7 \times 10^4 \sim 7 \times 10^5 \), around 2 for \( Pr = 2000 \) and \( RePr = 5 \times 10^5 \sim 9 \times 10^4 \) and around 0.35 for \( Pr = 5 \) and \( RePr = 7 \times 10^4 \sim 7 \times 10^5 \).

These discrepancies might result from the method of determination of the bulk liquid temperature. The extent of backmixing must be considered in the flow system for the rigorous determination of the effective temperature difference.

6.2.2 Investigations \( *) \) with pseudoplastic non-Newtonian fluids

It has been studied for the anchor agitator by Mizushima and Murakami (1966)\(^{[13]}\), Hagedorn\(^{[14]}\) et al. (1967) and Pollard\(^{[15]}\) et al. (1969). Mizushima and Murakami obtained in "turbulent region" (termed for convenience)

\[
\frac{h_j D}{\lambda} = 0.4 Re^{1/3} Pr^{1/2} (m_p/m_w)^{0.14}
\]

\[
\nu_v = \frac{m_p}{\pi D D / d} \left( 1 - \frac{2 \pi N}{D / d - 1} \right)^{-n}
\]

\[
8 \times 10^3 > Re > 300, \quad 1.0 > n > 0.45
\]

\( *) \) Here, \( m, n \) are correlated as to power law (shear stress) = \( m \) (rate of shear),

which is plotted in Fig. 21. The validity of \( Re^* \)
introduced here is confirmed by comparing the

[Fig. 21]
experimental data on which Eq. (30) is based with the correlation for Newtonian case, Eq. (31), with \( Re^* \) substituted for \( Re \) as shown in Fig. 22.

\[
\frac{Nu (\mu / \mu_b)^{b/14} (d/D)^{8/13}}{(b \sin \theta / H)^{8/13} (\eta_b)^{8/13} T_j} = 0.46 \frac{Re^{13/13} Pr^{13/13}}{Re_s = d^2 N2^{-n} \rho / m_b}
\]

\[
Re = (d^2 N2^{-n} \rho)^{1/3 (2n+1)} (0.92)^{3(1-n)/(2n+1)}
\]

\[
Pr = Re_s^{3/(2n+1)} (0.92)^{3(1-n)/(2n+1)}
\]

(32) - a

\[
\frac{Nu \left( \mu / \mu_b \right)^{b/14} (d/D)^{8/13}}{(b \sin \theta / H)^{8/13} (\eta_b)^{8/13} T_j} = 0.46 \frac{(1-n)}{(2n+1)} \left( Re_s \right)^2 + \frac{2(1-n)}{3(2n+1)}
\]

(33) - b

Eq. (34) was derived for "laminar region" (termed for convenience) based on the consideration of an analogy with the boundary layer flow on a flat plate. Fig. 24 shows a comparison with the experimental values where a qualitative agreement is observed.

\[
\frac{Nu \left( \mu / \mu_b \right)^{b/14} (d/D)^{8/13}}{(b \sin \theta / H)^{8/13} (\eta_b)^{8/13} T_j} = 4\left(\frac{C_s}{\mu / \mu_b}\right) \frac{1-n}{6n} \left( \frac{n+1}{2} \right)^{2/3} \frac{37}{1260} \frac{3(n+1)}{2n+1}
\]

\[
\times \left( \frac{28}{D/d-1} \right)^{1/(n+1)} Re^* \frac{1}{2} + \frac{(1-n)}{6(1+n)}
\]

\[
C(n) = \left( \frac{37}{1260} \frac{3(n+1)}{2n+1} \right)
\]

(34)

Eq. (34) can be simplified to

\[
h_{\text{ij}} D = \phi(n, D/d) Re^{n/2} (1-n) / 4(1+n) Pr^{n/3}
\]

\[
\times \left( \frac{\mu / \mu_b}{\mu / \mu_b} \right)^b
\]

(35)

\[
\phi(n, D/d = 1.18) = 0.78 n + 0.27
\]

when $D/d=1.18$

Hagedorn et al. obtained Eq. (36) similar to Eq. (35) for the pseudoplastic power law fluids and discussed other types of agitators such as paddles, turbines and propellers as well.

$$Nu=C(Re)^{ \frac{1}{2n-1}}(Pr_l)^{c}(m_l/m_b)^{d}(D/d)^{f}(b/d)^{f_s}$$

$$Re_s=d^2N^{2-n} \rho/m_b \quad Pr_s=C_p m_b N^{n-1}/\lambda$$  

(36)

$C=0.56 \quad a=1.43 \quad d=0.34 \quad c=0.3 \quad g=0.54$

$e=f=b=0$ ($e$ and $f$ were not tested)

$\frac{D}{d}=1.56$

Fig. 25 shows the correlated result. The ranges of variables studied are $Re_c=38 \times 10^3$ and $Pr_c=2 \sim 2.36 \times 10^4$ Mizushima and Murakami covered $Re_c=40 \sim 6 \times 10^3$ for non-Newtonian case and $Re_c$ up to $10^4$ for Newtonian case. The coefficient of 14 in the defining equation of apparent viscosity, Eq. (30), was determined on an empirical basis but a comparable result is seen in the newly defined $Re_c$, Eq. (33) - a. The procedure used for correlation by pollard et al. is as follows.

(1) First, establishing Eq. (37) for Newtonian fluid corresponding to Eq. (23)

(2) Determination of the relationship between shear rate and apparent viscosity of sample fluid.

(3) Calculation of the apparent viscosity, hence $Re_c$ and $Pr_s$, for a set of experimental conditions using the relationship between average shear rate and rotational speed. In his case

$$\tau \sim (\frac{1}{sec}) = 32 N^{2.75}$$

for $N > 0.8$

where $N$ is in r.p.s.

(4) Estimation of $Nu$ from Eq. (37).

This procedure gives a good agreement as shown in Fig. 26.

6.2.3 Comparison between various investigators

Three proposed correlations (Mizushima and Murakami, Hagedorn et al. and pollard et al.) are compared in Fig. 27 with experimental results by
Mizushina and Murakami. Fig. 28 shows another comparison in terms of \( R_e \). Fig. 29 shows the dependences of \( \gamma \) on \( N \) proposed by Pollard et al. and others, resulting in much discrepancies between them due to unclear reason. The followings are to be noted for quantitative discussion. As for apparatus, only Mizushina and Murakami separated the condensing chamber into two compartments. There is sometimes large variation in fluid properties due to aging (See Fig. 30). It is usual to compare the obtained correlation with the available one which is expected to be the most reliable. Mizushina and Murakami conducted the experiments under the same condition as that of Chilton and obtained Fig. 31, which indicates a good agreement between both workers. They also showed Eq. (23) to agree with Uhl’s results to within 3%. An comparison of Chilton’s data with Eq. (37) proposed for paddle by Hagedorn yields Fig. 32, resulting in \( \sim 50\% \) high calculated values than experimental.
\[ Nu = 2.51Re^{0.63}Pr^{0.28} (\mu_b/\mu \omega)^{0.31} (D/d)^{-0.16} (b/d)^{-0.46} \]  

(37)

Pollard et al. proposed Eq. (38) for anchor type, which gives lower values than the results of Uhl et al. and Mizushima and Murakami. However, these informations are not sufficient to explain the abovementioned difference.

\[ \frac{h_d}{D} = 0.35 \quad Re^{1/2}Pr^{1/3} (\mu_b/\mu \omega)^{0.14} \]  

(38)

6.3 Heat transfer studies with helical ribbon
A work by Mizushima et al. is available but only for Newtonian fluids. (Fig. 33) The proportional constants are 1.38 for laminar region and 0.52 for turbulent region which are somewhat large than corresponding values of 1.1 and 0.4, respectively, for anchor agitator. It is not clear if it is due to the circulating flow by helical ribbon.

**Nomenclature**

\[ A = \text{Surface area of liquid of DU} \quad [\text{cm}^2] \]

\[ a = \text{Surface area of liquid per unit volume} \quad [\text{cm}^2/\text{cm}^2] \]

\[ C = \text{A constant} \quad (= N_p \cdot Re) \quad [-] \]

\[ C_p = \text{A Constant} \quad (= \sqrt{Pe g_s f / \mu / n}) \quad [-] \]

\[ C_t = \text{A constant} \quad (= n \cdot T_M) \quad [-] \]

\[ C_s = \text{A constant} \quad (= T_M \sqrt{Pe g_s f / \mu}) \quad [-] \]

\[ C^* = \text{Equilibrium concentration of CO}_2 \text{ in liquid} \quad [\text{cm}^3/\text{cm}^3] \]

\[ C_D = \text{Initial concentration of CO}_2 \text{ in liquid} \quad [\text{cm}^3/\text{cm}^3] \]

\[ c = \text{Clearance between moving part and fixed wall} \quad [\text{cm}] \]

\[ D = \text{Diameter of vessel or tube} \quad [\text{cm}] \]

\[ D_d = \text{Diameter of disk of DU} \quad [\text{cm}] \]

\[ D_p = \text{Diffusivity in liquid phase} \quad [\text{cm}^2/\text{sec}] \]

\[ d = \text{Diameter of impeller} \quad [\text{cm}] \]

\[ f = \text{Friction factor} \quad [-] \]

\[ g_c = \text{Gravitational conversion factor} \quad [\text{g cm}/\text{G sec}^2] \]

\[ K_L = \text{Liquid phase mass transfer coefficient} \quad [\text{cm}/\text{sec}] \]

\[ L_o = \text{Scale of fluid element at original state} \quad [\text{cm}] \]

\[ L_M = \text{Scale of fluid element at final state of mixing} \quad [\text{cm}] \]

\[ L_{MF} = \text{Scale of fluid element calculated by Eq. (11)} \quad [\text{cm}] \]

\[ I_M = \text{Scale of fluid element calculated by Eq. (8)} \quad [\text{cm}] \]

\[ l = \text{Distance between disks of DU} \quad [\text{cm}] \]

\[ M = \text{Net amount of shear supplied} \quad [-] \]

\[ M_f = \text{That calculated by flow pattern analysis} \quad [-] \]

\[ M_g = \text{That calculated by power consumption} \quad [-] \]

\[ M_l = \text{Rate of shear} \quad [1/\text{sec}] \]

\[ M_{l1} = \text{Average rate of shear in region 1} \quad [1/\text{sec}] \]

\[ M_{l2} = \text{Average rate of shear in region 2} \quad [1/\text{sec}] \]

\[ m = \text{Coefficient of power law} \quad [\text{dyne cm}^2/\text{sec}] \]

\[ N = \text{Rotational speed (in section 6)} \quad [1/\text{sec}] \]

\[ N_c = \text{Total number of revolution of impeller} \]
required in one circulation

\( N_a \) = Axial circulation coefficient (flow rate/nd²) \( [-] \)

\( N_\theta \) = Tangential circulation coefficient like \( N_a \) \( [-] \)

\( N' \) = Rate of gas absorption \( [\text{cm}^3/\text{cm}^2 \text{ sec}] \)

\( n \) = Rotational speed (in section 1–5) \( [1/\text{sec}] \)

\( n = \) Coefficients of power law (in section 6) \( [-] \)

\( P \) = Power consumption \( [\text{G cm/sec}] \)

\( P_v \) = Power consumption per unit volume \( [\text{G cm/sec cm}^3] \)

\( P_v^* \) = Dimensionless that \((P_v \cdot \sqrt{\nu D}) \) \( [-] \)

\( S_{1,6}, S_{1,4} \) = The rate of surface renewal, observed that and estimated that, respectively \( [\text{cm}^2/\text{sec}] \)

\( T_M \) = Mixing time \( [\text{sec}] \)

\( t \) = Absorption time \( [\text{sec}] \)

\( t_{1,2} \) = Time taken in one circulation \( [\text{sec}] \)

\( t_1 \) = Mixing time in region 1 \( [\text{sec}] \)

\( t_2 \) = Mixing time in region 2 \( [\text{sec}] \)

\( \bar{u} \) = Average velocity in tube \( [\text{cm/sec}] \)

\( V \) = Liquid volume \( [\text{cm}^3] \)

\( v_r \) = Radial velocity of fluid \( [\text{cm/sec}] \)

\( v_r \) = Axial velocity of fluid \( [\text{cm/sec}] \)

\( v_\theta \) = Tangential velocity of fluid \( [\text{cm/sec}] \)

\( v_\theta \) = Blade tip velocity \( (= \cdot n_d) \) \( [\text{cm/sec}] \)

\( x \) = Ratio of impeller diameter to vessel one \( [-] \)

\( \mu \) = Liquid viscosity \( [\text{poise}] \)

\( \rho \) = Density of liquid \( [\text{g/cm}^3] \)

\( \delta_r \) = Diffusion thickness \( [\text{cm}] \)

\( N_p \) = Power number \( (= \rho g \cdot \nu n^2 d^4) \) \( [-] \)

\( Re \) = Reynolds number \( (= \rho n d^2/\mu) \) (for mixing)

\( (= \rho \bar{u} D/\mu) \) (for tube flow) \( [-] \)

**Subscripts**

\( b \) = Bulk temperature

\( w \) = Wall temperature

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**Literature Cited**


2. Kajimoto, H.; Private communication

3. Shimada, T.; Private communication


