Mixing Problems for High Viscosity Fluids in polymer Production Processes

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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 $C_1 = nT_M$ and the shearing amount, $C_2 = T_M \sqrt{P_v\ g_c/\mu}$ 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 chracteristics. 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

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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 futher 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 them 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

Final React	By Product	Tm(°C)	(K)	Process	Poly Stages	Poly (HR)	T(°C)	P (mmHg)	μ (Poise)
$HO-[CH_2CH_2OOC-\bigcirc-COO]_n$ CH$_2$OH / $HO[CH_2CH_2OOC-\bigcirc-COO]_m$ CH$_2$CH$_2$OH $+nHOCH_2CH_2OH$	HOCH$_2$CH$_2$OH	260~270	4~5	BY PRODUCT VAPOR (*) PREPOLYMERIZER / ESTER INTERCHANGE COLUMN / SCRAP POLYMER / FINISHER / PUMP / FILTER	1	4~6	160~220	760	
					2	2~3	265~285	10~100	100
					3	7~	265~285	<10	2000~2500
$nNH_2(CH_2)_6 NH_2+nHOOC(CH_2)_4 COOH$ $\rightarrow H_2N[(CH_2)_6 NHCO(CH_2)_4 CO]_n OH$ $+(2n-1)H_2O$	H$_2$O	260~270	900~500	MATERIALS / PREPOLYMERIZER / HEAT EXCHANGER / PREPOLYMER / FINISHER / POLYMER PUMP	1	Total 3Hr	100~230	17.5 atü	
					2		275	0 atü	1000~2000
$nH_2NCONH_2 +nH_2NRNH_2$ $\rightarrow [RNHCONH]_n + NH_3$	NH$_3$	287		MATERIALS / PUMP / PREPOLYMERIZER / FINISHER / PUMP	1	2~3	100~120	>1 atm	
					2	2~			
					3	~1	240~260	10~20	2000~2500
(polycarbonate structure)	OH	220~230			1	0.5~1	180~200	50	
					2	0.5~1	200~220	15	
					3	3~4	220~270	1	3000~5000

tons of polymer produced
(by a particular type of reactor)
(100 tons of total production)

Table 1.

	Stirred tank	Tower	Special type
	(wt%)		
Polymer industry (total) (Plastic, Synthetic fibre Rubber)	90	10	2
Synthetic fibre industry	70	30	7

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 inpolymerizing systems from two main considerations. The first is related to the problem of heat removal and the reaction conversion. In vinyltype 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 thicness 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 trantsfer 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 petched 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. Fof horizontal sections, the camera and the impeller were synchronously rotated in order to observe the
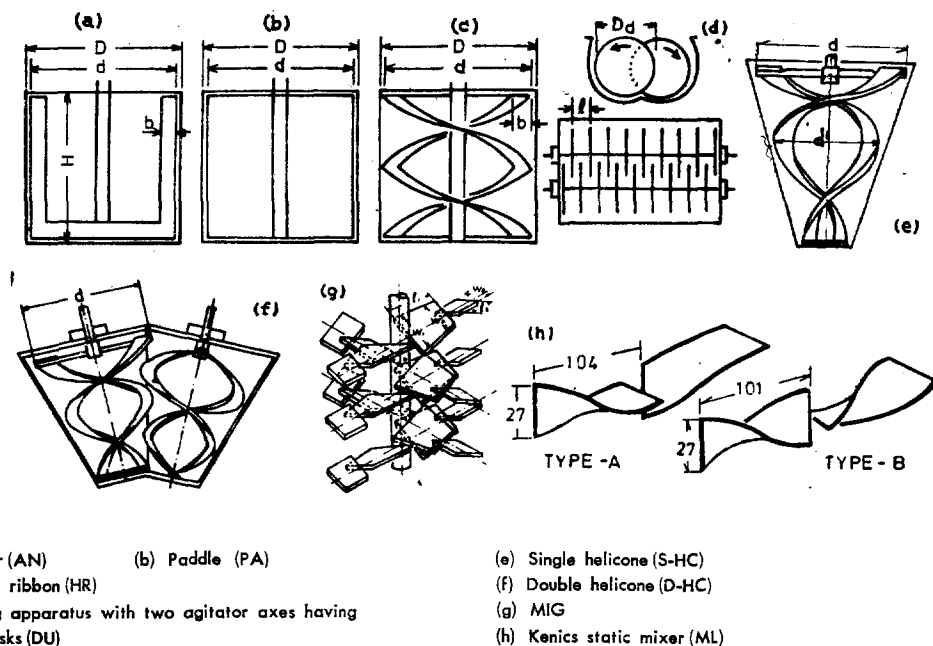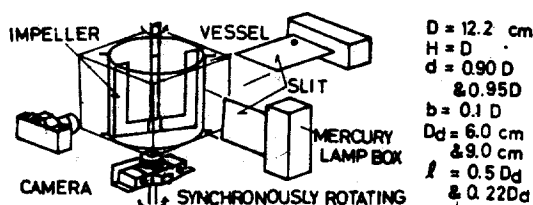

(a) Anchor (AN)   (b) Paddle (PA)
(c) Helical ribbon (HR)
(d) Mixing apparatus with two agitator axes having
     multidisks (DU)

(e) Single helicone (S-HC)
(f) Double helicone (D-HC)
(g) MIG
(h) Kenics static mixer (ML)

Fig. 1 Impellers and Vessels

Fig. 2 Directions of Camera and slit Ray

D = 12.2 cm
H = D
d = 0.90 D
& 0.95D
b = 0.1 D
D_d = 6.0 cm
& 9.0 cm
ℓ = 0.5 D_d
& 0.22D_d

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_z. 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

Fig. 5 Helical ribbon (velocity profiles)

Fig. 6 Du pont type miixer (velocity profiles at the section of 6mm apart from the disk at 15mm space intervals)

Fig. 3 Anchor (stream lines and tangential velocity profiles)

Fig. 4 Paddle (stream lines and tangential velocity profiles)

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
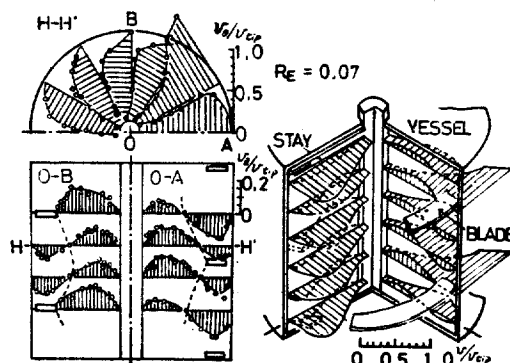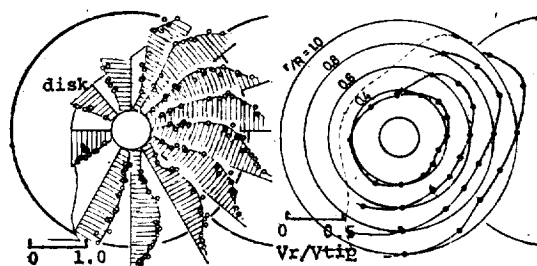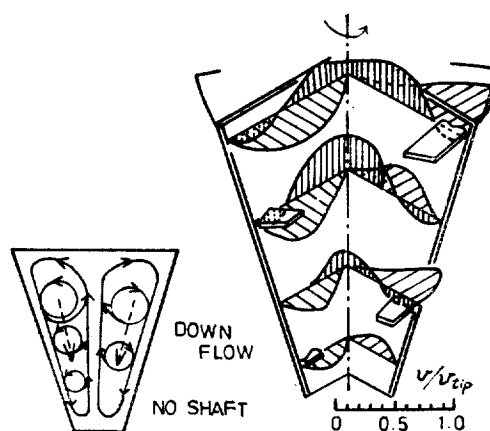

Fig. 7 Flow patterns of single helicone

should be noted that the essential exchanges in a radial direction hardly exist because of a creeping flow as shown in Fig. 3.

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 agiatator 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 equiped with assembled
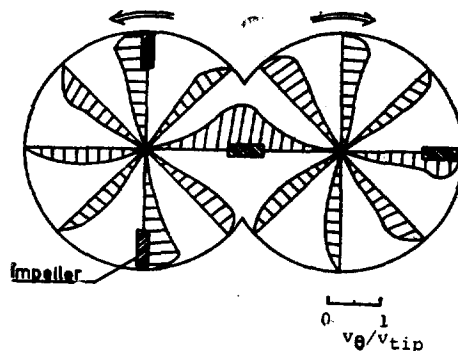

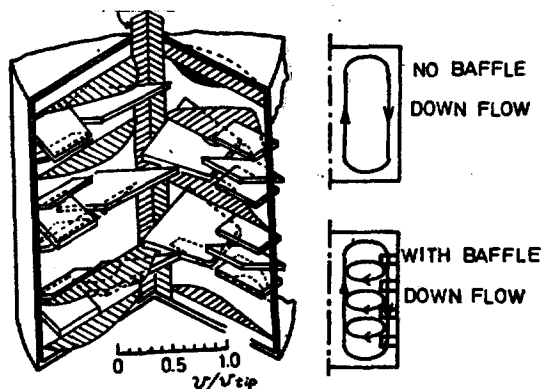
Fig. 8 Flow patterns of double helicone
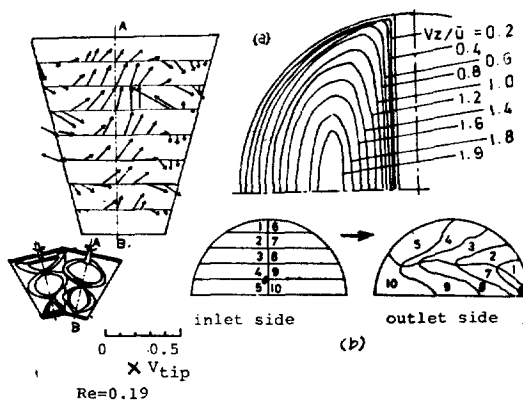

Fig. 9 Flow patterns of MIG

Fig. 10 (a) Curves of constant velocity for ML
(b) Change of position per mixing unit

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

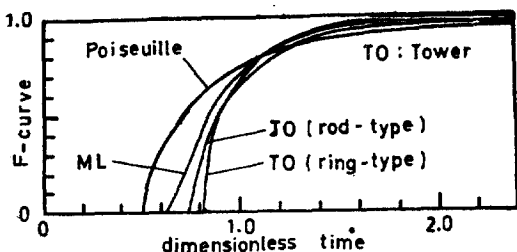approached as shown in Fig. 11. A displacement

Fig. 11 Residence time distribution curves

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.

$$Pvg_c/\mu$$

$$= 2\left\{\underbrace{\left(\frac{\partial v_r}{\partial r}\right)^2}_{A} + \left[\frac{1}{r}\left(\frac{\partial v_\theta}{\partial \theta} + v_r\right)\right]^2 + \left(\frac{\partial v_z}{\partial z}\right)^2\right\}$$

$$+ \left\{\underbrace{\left(\frac{\partial v_\theta}{\partial z} + \frac{1}{r}\frac{\partial v_z}{\partial \theta}\right)^2}_{H} + \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial_z}\right)^2\right.$$

$$\left.\underbrace{+\left[\frac{1}{r}\frac{\partial v_r}{\partial \theta} + r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right)\right]^2}_{\substack{A.P. \\ H}}\right\} \qquad (1)$$

Fig. 12 shows the distributions in a given
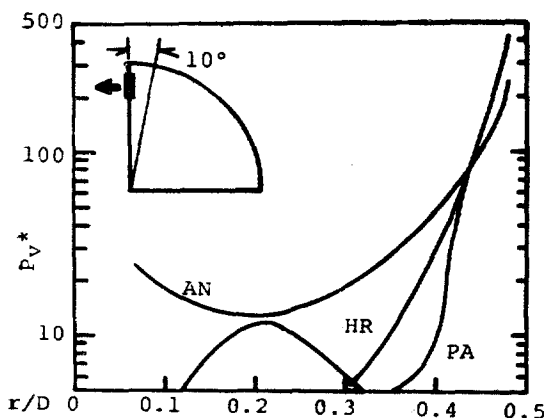
Fig. 12 Distribution of dissipation energy for PA, AN and HR

ANCHOR   PADDLE   HELICAL RIBBON

Pv^* ☐ 0-5 ▨ 5-10 ☱ 10-20 ⊠ 20-30 ▬ 30-100 ▦ 100-
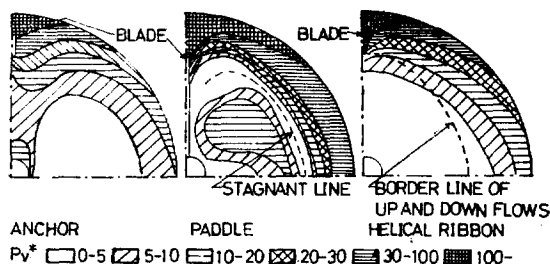
horizontal section. It becomes clear that the high shear region is maldistributed near the blade. Consequently, for high viscosity apparatus it is a problem how the fluid moves into and out of high shear region.

In Eg. (1), underlined terms A, P and H are dominant ($>80\sim90\%$) 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 3. Mixing Time and circulation Capacity

Impeller	Nq	Nqz	Nc	3Nc	nT_M[1]
Anchor	0.37	0	—	—	—
Ribbon	0.37	0.081	11	33	33
Screw with draft tube	—	0.42	14	42	45

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 vitcosity 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.

$$Lo/L_M = M = \dot{M} T_M (M \gg 1) \tag{2}$$

where Lo and L_M are the scale of fluide 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 κ of the inner diameter to the outer one is assumed as $\kappa \simeq 1$, the shear rate becomes $M = 2\pi kn/(1\text{-}k)$. Therefore Eq. (2) gives the following relation for mixing time.

$$n T_M = (Lo/L_M) \left[(1-\kappa)/2\pi\kappa \right] \tag{3}$$

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

$$\sqrt{Pvgc/\mu} = 4\pi\kappa n/(1-\kappa^2) \tag{4}$$

From Eqs. (3) and (4),

$$T_M \sqrt{Pvgc/\mu} = \left[2/(1+\kappa) \right] (Lo/L_M) \tag{5}$$

The above relation seems to explain a physical meaning of $T_M \sqrt{Pvgc/\mu} = $const., that is, the term $2/(1+\kappa)$ may be a constant depending of a geometrical configuration of an apparatus and the term L_O/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 homoginizing process could be thought to be ideal. The ideal limit of $T_M \sqrt{Pvgc/\mu}$ may be equal the scale ratio L_O/L_M.

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

$$n T_M = C_1 \text{ (const.)} \tag{6}$$

$$T_M \sqrt{Pvgc/\mu} = C_2 \text{ (const.)} \tag{7}$$

Table 4. Mixing Characteristics

Types of mixers	C $[NpRe]$	Co $[\sqrt{Pvgc/\mu/n}]$	C₁ $[nT_M]$	C₂ $[T_M\sqrt{Pvgc/\mu}]$
Helical ribbon (Nagata[1])	300	18.1	33	600
Helical ribbon (Gray[3])	413	19.6	25.3	500
Helical screw (Nagata[1])	200	8.4	45	400
Helical screw (Gray[3])	416	4.1	220	900
DU	—	12~24	39~46	550~940
MIG (no baffle)	240	16.2	48	776
MIG (baffles)	330	19.0	33	625
S-HC (down flow)	260	23.3	25	581
S-HC (up-flow)	350	27.0	25	675
D-HC (down flow)	690	24.7	20.5	506
ML (type A)	—	8.4	44	370
ML (type B)	—	8.5	34	290

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 $\sqrt{Pvgc/\mu}$ that the shear action is dominant in mixing devices. The authors considered

a heilcal 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 Mp of T_M by $\sqrt{P_{\mathrm{vgc}}/\mu}$ from power consumption, and the other is the product M_f of T_M by $\dot{M}$ from the flow pattern as follows.

$$Mp=19.3\ n T_M \quad (8) \qquad M_f=N_C(\dot{M}_1 t_1+\dot{M}_2 t_2) \qquad (9)$$

$$T_M=N_C(t_2+t_1) \qquad (10)$$

where

$$t_1=t_2$$

$$\dot{M}_1=18.6\ n, \quad \dot{M}_2=4.0\ n$$

$$M_f=11.3\ n T_M \qquad (11)$$

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

$$\dot{M}_{12}=\int_S \dot{M} v_z\ ds/\int_S v_Z\ ds \qquad (12)$$

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.
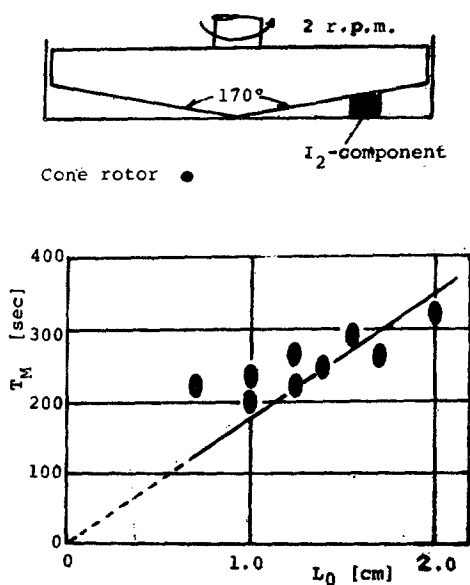

Fig. 13 Mixing time and initial scale

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 mixor is shown in Fig. 13 and the measurement of mixing time is carried out by a method[1] of reaction of I_2-$Na_2S_2O_3$, in which a minor component is I_2-corn syrup solution, 15.5g I_2/kg corn syrup solution, and a major component is $Na_2S_2O_3$-corn syrup solution, 15.4g $Na_2S_2O_3 \cdot 5H_2O$/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 reactionis 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 $L_M=0.0018$ cm although the judge is fairly delicate. The results for a helical ribbon are summarized in Fig. 13 and Tabe 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. Miling time and striation thickness for helical ribbon mixer

L_0[cm]	T_M[sec]	L_{MP}[cm]	L_{Mf}[cm]
0.07	230	1.18×10^{-3}	2.02×10^{-3}
1.00	236	1.65	2.81
1.00	200	1.96	3.32
1.23	225	2.08	3.63
1.23	268	1.79	3.05
1.40	245	2.22	3.79
1.57	290	2.11	3.59
1.70	260	2.54	4.34
2.00	317	2.45	4.19
		av. 2.00×10^{-3}	3.42×10^{-3}

There becomes $L_{MP}=0.0020$ cm by Eq. (8) and $L_{Mf}=0.0034$ cm by Eq. (11). On comparing two values, the scale L_{MP} from the power consumption has a fairly good aqreement with the scale L_M of a

cone rotor mixer.

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[2] of Mitsubishi Heavy Industries Ltd., and the authors take $\sqrt{Pvgc/\mu}/n$ or $D\sqrt{Pvgc/\mu}/\bar{u}$ 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 κ 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
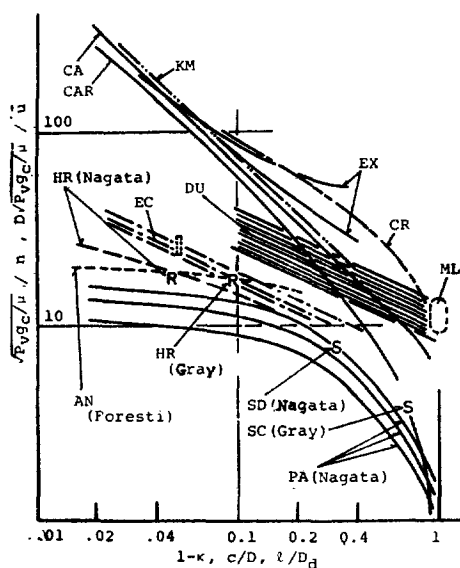
disks to the disk diameter for an apparatus with two agitator axes having multidisks. These ratios can be considered to be one criterion of shear field.

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[3]-kajimoto, gives information as to mixing time and power consumption for various kinds of mixing equipment used in the range of laminar region.
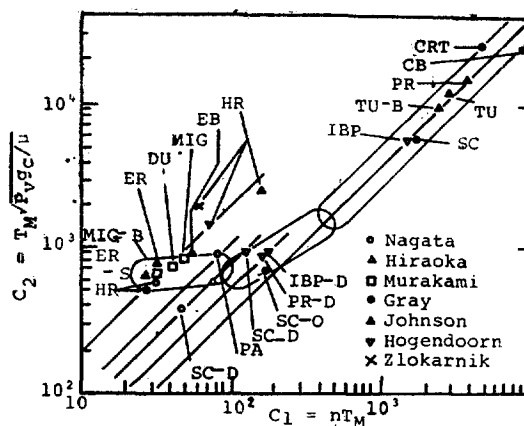

Fig. 15 Mixing characteristics[3]
CB-Curved blade, CRT-Curved rod & turbine, EB-Elliptic boad, ER-Elliptic ribbon, IBP-Inclined blade paddle, PR-Propeller, SC-Screw, TU-Turbine,
(—S)—with screen, (—D)—with draft tube,
(—B)—with baffle, (—O)—off centered

4. Homogenizing Characteristics of Kenics Type Motionless Mixer

Brunemann[4] studied for some kinds of static mixer. 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.

Fig. 14 Shear characteristics[2]
CA-Circular annulus, CAR-Circular annulus rotating cylinder, CR-C & R reactor, EC-Eccentrical cylinders, EX-Extruder, KM-Keilspltmachinen

Fig. 16 Striation thickness variation in Kenics type motionless
mixer ($\bar{u}$=0.14 cm/sec, 200 poises)

For motionless mixer, $Pvgc$ is calculated as follows.

$$Pvgc = 2f\rho\bar{u}^3/D \qquad (13)$$

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

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

Experimental results are summarized in Table 4. The value of C_2 for double helical ribbon mixer is about two times that for kenics type motionless mixer. This relation tells that a limitting value of C_1 is about C_1 limit=16 (=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

$$N' = Va\sqrt{DvS}(C^* - C_0)\ \exp\ (-a\sqrt{DvS}\ t) \qquad (15)$$

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

$$K_La = a\sqrt{D_vS} = 0.58_n{}^{1/3}{}_v{}^{-3/2} \qquad (16)$$

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

$$a = 2.02 \times 10^4\ n^{-1/6}\ v^{-2} \qquad (17)$$

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

$$S_{obs.} = 4.12 \times 10^{-3}nV \qquad (18)$$

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.

$$S_{est.} = 2\ v_mL/A \qquad (19)$$

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

$$V_m = 4.2\ n \qquad (20)$$

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

$$S_{est.} = 3.95 \times 10^{-3}n^{7/6}V \qquad (21)$$

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 buld 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, δc, for nylon 66 have no trouble in considering as about $\delta c = 10^{-1} \simeq 10^0$ cm. When the order of a boundary layer thickness is estimnted by $2\sqrt{2D_V t}$ (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 $D_V \simeq 10^{-5}$ cm²/sec for the order of diffusivity coefficient for byproduct.

$$S = t^{-1} \simeq 8 D_V \delta_C{}^{-2} = 8 \times 10^{-5} \times 1.0^{-2} \sim 8 \times 10^{-5} \times 0.1^{-2}$$
$$= 8 \times 10^{-5} \sim 8 \times 10^{-3} \sec^{-1}$$

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 polycondenstaion reaction characteristics alone. On the pontrary, polyethylene terephthalate polycondensation has very small value of equilibrium constant, about $10^{-2} \times$ (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 polycondensation reaction has to be $10^{-2} \times$ (the order of liquid thickness of diffusion for nylon 66), then.

$S = [8 D_V \delta_c{}^{-2}]_{\text{nylon}} 66 \times 10^4 = 0.8 \sim 80 \sec^{-1}$, which value gives a suggestion that a rate determing state. From above mentioned discussions, engineering considerations for nylon 66 are restricted to the problem concerning with completion of the reaction.

6, Some Aspect 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[5] (1960) reviewed those investigations up to 1959. Chapman[6] (1965) gave a review of literature up to 1963, which is concerned with low viscosity Newtonian fluids. Ito[7] (1963) discussed non-Newtonian heat transfer and gave useful recommendations. "Mixing" edited by Uhl[8] 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[9] et al. should be referred to where the coloseclearance 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 dose not have the clear physical meaning.

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

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

$$Nu = a \left(RePr^{\frac{1}{2}} + b\right)^{\frac{2}{3}} (vb/vw)_m \qquad (22)$$

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 Mizushina and Murakami[11] as follows
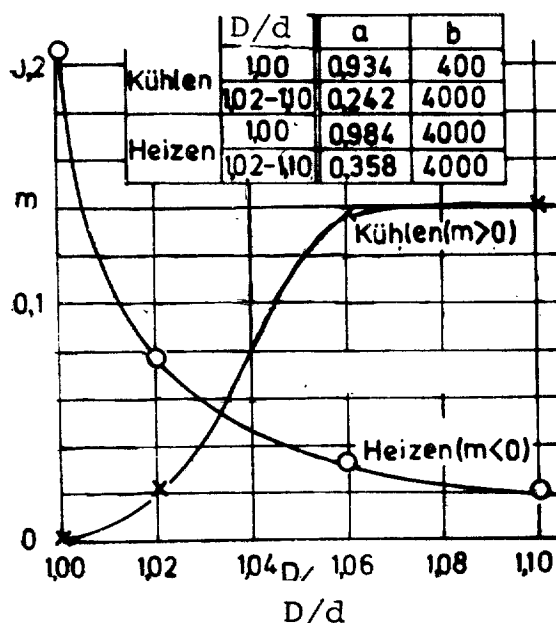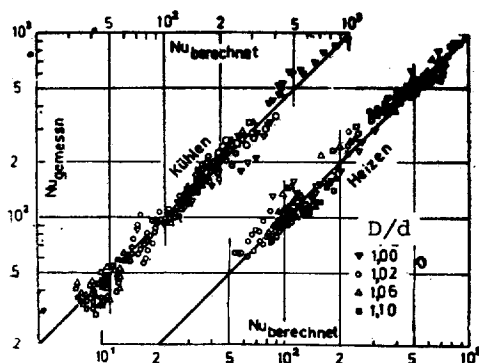
D/d		a	b
Kühlen	1,00	0,934	400
	1,02-1,10	0,242	4000
Heizen	1,00	0,984	4000
	1,02-1,10	0,358	4000

Fig. 17

Fig. 19

Fig. 18

$$Nu = 0.4\ Re^{2/3} pr^{1/3} (\mu b/\mu w)^{0.14} \quad \text{for } Re > 300 \qquad (23)$$

Zlokarnik employed the unsteady state technique while Mizushina, Murakami, the steady state one. A numerical comparison as shown in Fig. 19 shows an subtantial 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 is 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[12] pointed out the significance of the flow pattern and eddies formed in the vicinity of the agetator in the batch operation of anchor agitator with high viscosity liquid as schematically
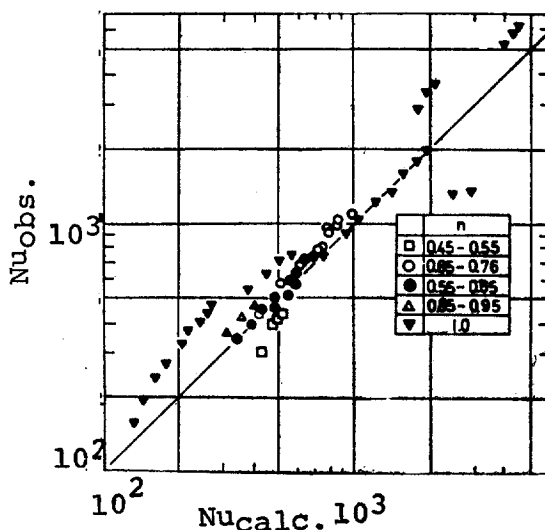
visualized in Fig. 20. He recommended the anchor agitator for Re>300 where the following equation can apply

Fig. 20
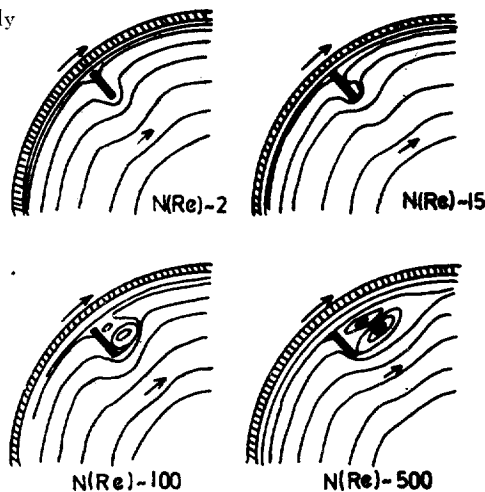
$$\frac{h_j D}{\lambda} = K Re^{2/3} pr^{1/3} \left(\frac{\mu b}{\mu w}\right)^{0.18} \qquad (24)$$

where

$\frac{1}{2}\left(1-\dfrac{d}{D}\right)$	0.01	0.02	0.03	0.04	0.06
K	0.38	0.38	0.38	0.42	0.47

He explained the increase in k with the clearance

due to the effect of disturbance formed near the agitator. Mizushina 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 Mizushina 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

$$K'=1.05 \text{ at } \frac{1}{2}\left(1-\frac{d}{D}\right)=0.076 \qquad \text{is given by}$$

Mizushina and Murakami. In case of pseudoplastic non-Newtonian fluid, the helical ribbon with scraper blades are recommended where $\bar{h}_j$ 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.

$$\bar{h}_j D/\lambda = K' Re^{1/2} pr^{1/3} (\mu_b/\mu_w)^{0.18} \qquad (25)$$

$$\bar{h}_j D/\lambda = 4/(1-d/D) \qquad (26)$$

$1/2(1-d/D)$	0.01	0.02	0.03	0.04	0.07
K'	1.2	0.9	0.9	1.0	1.3

Mizushina 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 Mizushina et al. [13]

$$(Nu)_1 = \frac{2\sqrt{2}}{\sqrt{\pi}} Re^{1/2} Pr^{1/2} \text{ (Mizushina, } n_p=2) \quad (27)$$

$$(Nu)_2 = 0.934(RePr^{1/2}+400)^{2/3} \text{ (Zlokarnik)} \qquad (28)$$

in which the constant, 400, is in turn negligibly small relative to the practical values of $RePr^{\frac{1}{2}}$ greater than 10^4. This simplification yields

$$\frac{(Nu)_1}{(Nu)_2}=1.71\left(\frac{Pr}{Re}\right)^{\frac{1}{6}} \qquad (29)$$

indicating that the ratio of $\frac{(Nu)_1}{(Nu)_2}$ is around unity for $Pr=500$ and $RePr^{\frac{1}{2}}=7\times10^4\sim7\times10^5$, around 2 for $Pr=2000$ and $RePr^{\frac{1}{2}}=5\times10^3\sim9\times10^4$ and around 0.35 for $Pr=5$ and $RePr^{\frac{1}{2}}=7\times10^4\sim7\times10^5$.

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

6.2.2 Investigations (*) with pseudoplastic non-Newtonian fluids

It has been studied for the anchor agitator by Mizushina and Murakami (1966) [11], Hagedorn [14] et al. (1967) and pollard [15] et al. (1969). Mizushina and Murakami obtained in "turbulent region" (termed for convenience)

$$\bar{h}_j D/\lambda = 0.4 Re^{*1/3} Pr^{*1/3} (m_b/m_w)^{0.14}$$
$$\mu_{aw}=m_b\left(14\cdot\frac{2\pi N}{D/d-1}\right)^{n-1} \qquad (30)$$
$$8\times10^5>Re^*>300, \quad 1.0>n>0.45$$

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

which is ploted in Fig. 21. The validity of Re^* introduced here is confirmed by comparing the
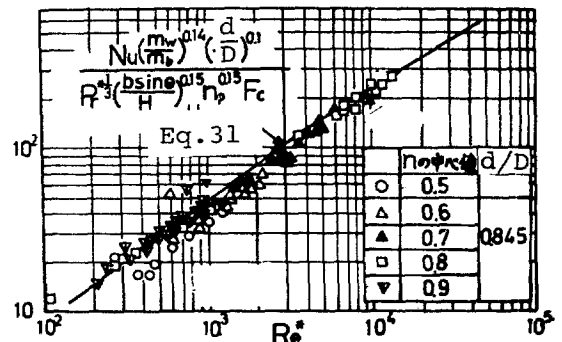

Fig. 21

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.
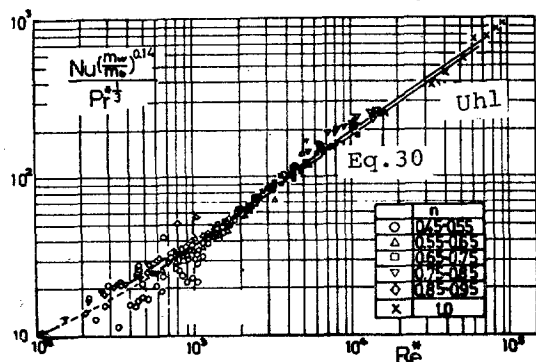

Fig. 22

For

$$(b \ \sin\theta/H) \geqq 0.315, \quad (b \ \sin\theta/H) = 0.315$$
$$\text{and} \ 4 \times 10^5 > Re > 10^2$$

$$\frac{(\bar{h}_j D - \lambda) \ (\mu_w/\mu_b)^{0.14} (d/D)^{0.1}}{(C_{p \ b}/\lambda)^{1/3} (b \ \sin\theta/H)^{0.15} (n_p)^{0.15} F_c}$$
$$= 0.85 \ (Re)^{1/2} (d/D)^{-0.4} + 0.45 \left(\frac{Re}{103 + 1.43 Re}\right) Re^{2/3}$$

$$(31)$$

where $Fc = 1$ usually in this system. Fig. 23 shows a comparison of experimental data in Fig. 21 with an extended Newtonian correlation which results from the substitution of newly defined Re and Pr (See Eq. (33)-a) introduced for the interpretation of momentum transfer into the conventional Newtonian correlation, Eq. (31).
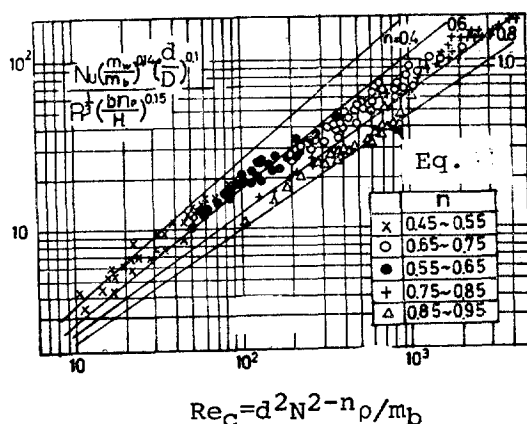
$$Re_c = d^2 N^{2-n} \rho/m_b$$

Fig. 23

$$\frac{Nu \ (\mu^w/\mu_b)^{0.14} (d/D)^{0.1}}{(b \ \sin\theta/H)^{0.15} (n_p)^{0.15}} = 0.46 \ Re^{2/3} Pr^{1/3}$$
$$Re_c = d^2 N^{2-n} \rho/m_b \qquad (32)$$

$$Re = (d^2 N^{2-n} \rho)^{3/(2n+1)} \ (0.92)^{3(1-n)/(2n+1)}$$
$$Pr = Pe \ Re_c^{-3/(2n+1)} \ (0.92)^{3(n-1)/(2n+1)} \qquad (33)\text{-a}$$

$$\frac{Nu \ (m_w/m_b)^{0.14} (d/D)^{0.1}}{(C_p m_b/\lambda N^{n-1})^{1/3} \ (b \ \sin\theta/H)^{0.15} (n_p)^{0.15}}$$
$$= 0.46 \ (0.92)^{-\frac{(1-n)}{(2n+1)}} (Re_c)^{\frac{2}{3} + \frac{2(1-n)}{3(2n+1)}} \qquad (33)\text{-b}$$

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.
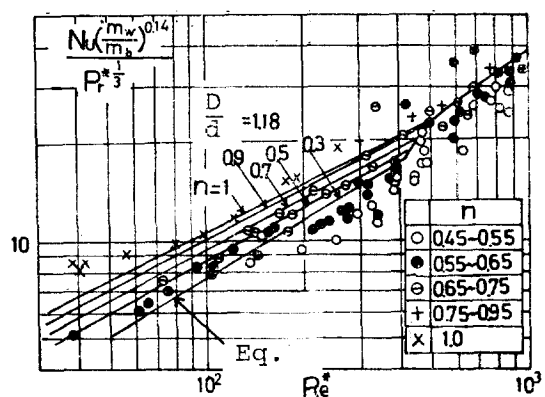

Fig. 24

$$Nu \ (m_w/m_b)^{0.14}/Pr^{*1/3}$$
$$= 4 \ (C_n)^{-\frac{1-n}{6n}} \left(\frac{n+1}{2}\right)^{-1/6} \sqrt{\frac{37}{1260} - \frac{3(n+1)}{2n+1}}$$
$$\times [D/2d]^{2n+1} \left(\frac{28}{D/d-1}\right)^{n-1]^{1/3(n+1)}} Re^{*\frac{1}{2} + \frac{(1-n)}{6(1+n)}}$$
$$C(n) = \left(\frac{37}{315} \frac{2}{n+1}\right)^{n/(n+1)} \qquad (34)$$

Eq. (34) can be simplified to
$$\bar{h}_j D/\lambda = \Phi(n, D/d) \ Re^{*1/2+(1-n)/6(1+n)} Pr^{*1/3}$$
$$\times (m_b/m_w)^{0.14}$$
$$\Phi\left(n, \frac{D}{d} = 1.18\right) = 0.78 \ n + 0.27$$

$$600 > Re^* > 40, \quad 1.0 > n > 0.45 \qquad (35)$$

when $D/d = 1.18$

Hagedorn[14] 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.

$$Nu = C (Re_c)^{\frac{a}{n+1}+b} (Pr_c)^c (m_b/m_w)^d (D/d)^e (b/d)^f n^g$$

$$Re_c = d^2 N^{2-n} \rho / m_b, \quad Pr_c = C_p m_p N^{n-1} / \lambda \qquad (36)$$

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

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

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

Fig. 25 shows the correlated result. The ranges of variables studied are $Rec = 35 \sim 6.8 \times 10^5$ and $Prc = 2 \sim 2.36 \times 10^4$ Mizushina and Murakami covered $Re = 40 \sim 6 \times 10^3$ for non-Newtonian case and Re up to 10^5 for Newtonian case. The cofficient 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, Eq. (33)-a. The procedure used for correlation by pollard et at[15]. is as follows.

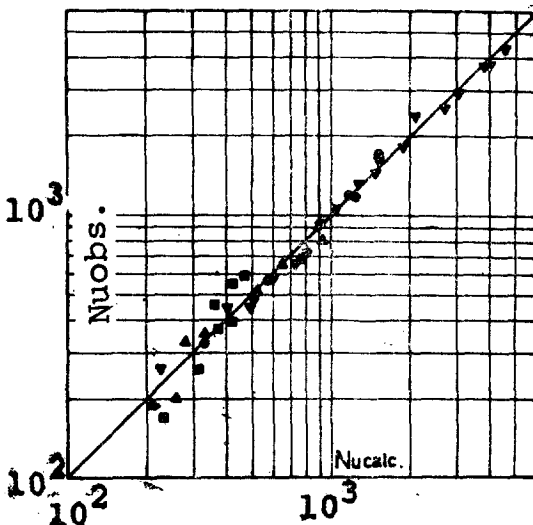Fig. 25

(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 and Pr, for a set of experimental conditions using the relationship between average shear rate and rotational speed. in his case

$$\dot{\gamma} \, av\left(\frac{1}{\sec}\right) = 32 N^{3.75} \text{ for } N > 0.8$$

where N is in r.p.s.

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

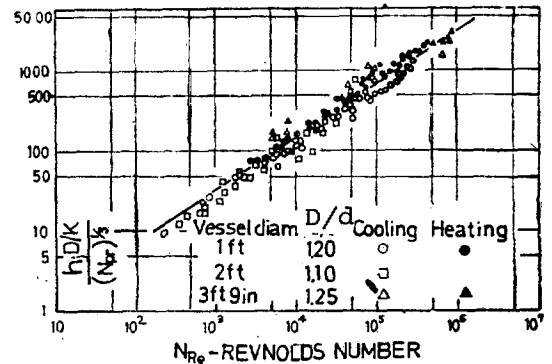This procedure gives a good agreement as shown in Fig. 26.

Fig. 26

6.2.3 Comparison between various investigators

Three proposed correlations (Mizushina and Murakami, Hagedorn et al. and pollard et al.) are compard in Fig. 27 with experimental results by
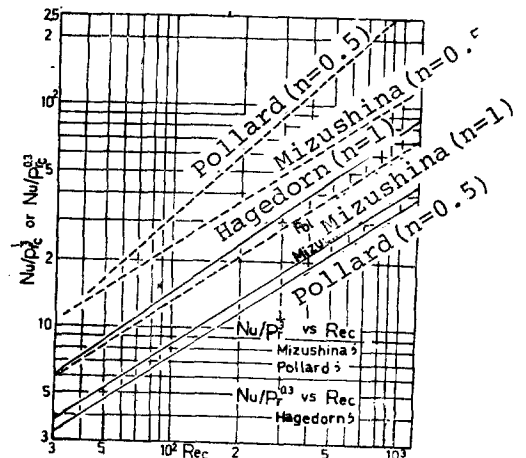

Fig. 27

Mizushina and Murakami. Fig. 28 shows another comparson in terms of *Rec*. Fig. 29 shows the dependences of γ *av*. 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 sithin 3%. An comparison of Chilton's data with Eq. (37) proposed for paddle by Hagedorn yields Fig. 32, resulting in ~50% high calculated values than experimental.
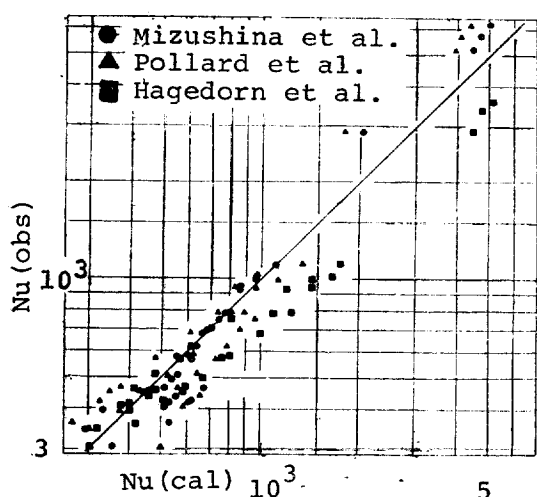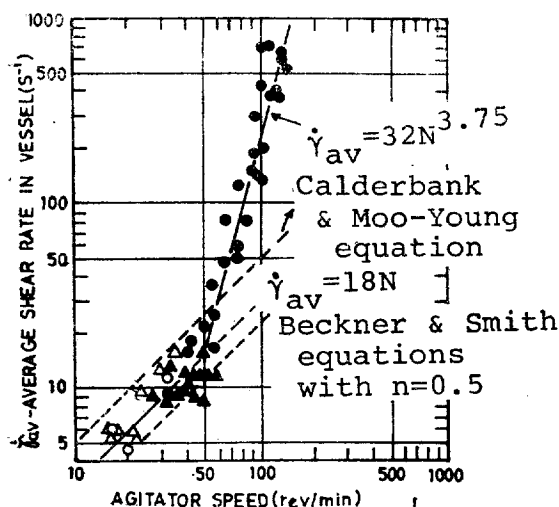

Fig. 28

Fig. 30

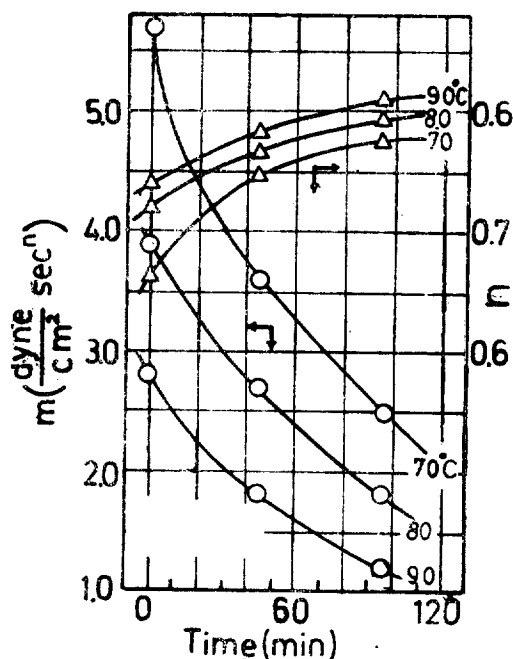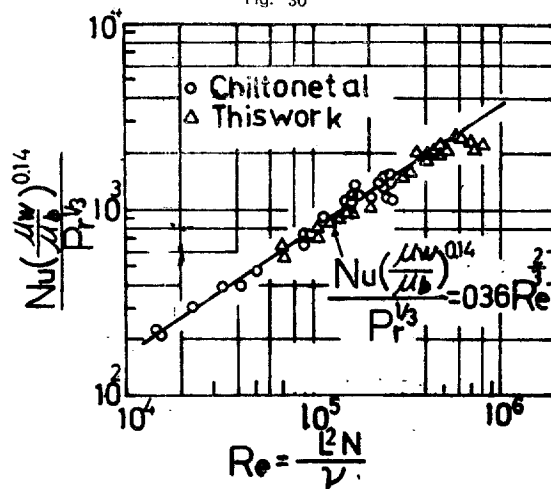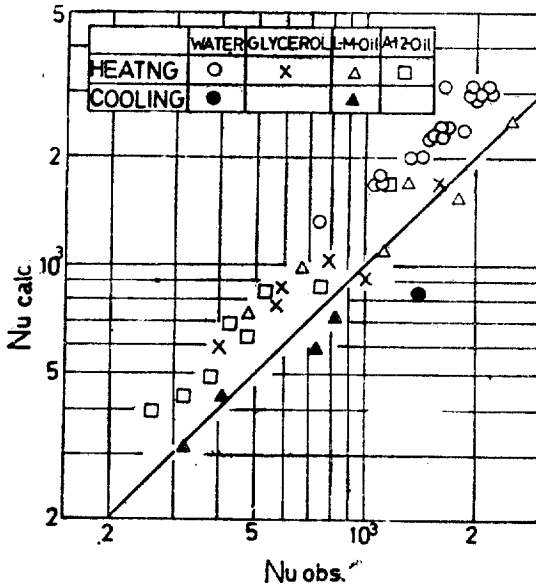

Fig. 29

Fig. 31

Fig. 32

$$Nu = 2.51 Re^{0.63} Pr^{0.26} (\mu b/\mu w)^{0.31} (D/d)^{-0.46} (b/d)^{-0.46}$$

$$(37)$$

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

$$\bar{h}_j D/\lambda = 0.35 \ Re^{2/3} Pr^{1/3} (\mu b/\mu w)^{0.14} \qquad (38)$$

6.3 Heat transfer studies with helical ribbon

A wrok by Mizushina et al. is available but only for Newtonian fluids. (Fig. 33) The proportional
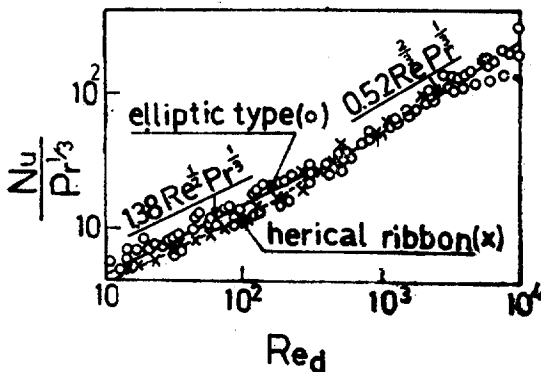

Fig. 33

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=Surface area of liquid of DU [cm²]

a=Surface area of liquid per unit volume

[cm²/cm³]

C=A constant $(=Np. Re)$ [—]

C_0=A Constant $(=\sqrt{P_v g_c/\mu}/n)$ [—]

C_1=A constant $(=n \cdot T_M)$ [—]

C_2=A constant $(=T_M \sqrt{P_v g_c/\mu})$ [—]

C^*=Equilibrium concentration of CO_2 in

liquid [cm³/cm³]

C_O=Initial concentration of CO_2 in liquid [cm³/cm³]

c=Clearance between moving part and

fixed wall [cm]

D=Diameter of vessel or tube [cm]

D_d=Diameter of disk of DU [cm]

D_v=Diffusivity in liquid phase [cm²/sec]

d=Diameter of impeller [cm]

f=Friction factor [—]

g_c=Gravitational conversion factor [g cm/G sec²]

K_L=Liquid phase mass transfer coefficient [cm/sec]

L_O=Scale of fluid element at original state [cm]

L_M=Scale of fluid element at final state of

mixing [cm]

L_{Mf}=Scale of fluid element calculated by

Eq. (11) [cm]

L_{Mp}=Scale of fluid element calculated by

Eq. (8) [cm]

l=Distance beween disks of DU [cm]

M=Net amount of shear supplied [—]

M_f=That calculated by flow pattern analysis [—]

M_P=That calculated by power consumption [—]

$\dot{M}$=Rate of shear [1/sec]

$\dot{M}_1$=Average rate of shear in region 1 [1/sec]

$\dot{M}_2$=Average rate of shear in region 2 [1/sec]

m=Coefficient of power law [(dyne/cm²) sec²]

N=Rotational speed (in section 6) [1/sec]

N_C=Total number of revolution of impeller

required in one circulation $[-]$

N_{qz}=Axial circulation coefficient (flow rate/nd³) $[-]$

$N_q\theta$=Tangential circulation coefficient like Nq_z $[-]$

N'=Rate of gas absorption [cm³/cm² sec]

n=Rotational speed (in section 1∼5) [1/sec]

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

P=Power consumption [G cm/sec]

P_v=Power consumption per unit volume

[G cm/sec cm³]

P_V^*=Dimensionless that $(P_v g_c/\mu\ (\pi nd/D)^2)$ $[-]$

S, S_{obs}, S_{est}=The rate of surface renewal, observed

that and estimated that, respectively

[cm²/cm²sec]

T_M=Mixing time [sec]

t=Absorption time [sec]

t_c=Time taken in one circulation [sec]

t_1=Mixing time in region 1 [sec]

t_2=Mixing time in region 2 [sec]

$\bar{u}$=Average velocity in tube [cm/sec]

V=liquid volume [cm³]

v_r=Radial velocity of fluid [cm/sec]

v_z=Axial velocity of fluid [cm/sec]

$v\theta$=Tangential velocity of fluid [cm/sec]

v_{tip}=Blade tip velocity ($=\pi$ nd) [cm/sec]

κ=Ratio of impeller diameter to vessel one $[-]$

μ=Liquid viscosity [poise]

ρ=Density of liquid [g/cm³]

δ_c=Diffusion thickness [cm]

Np=Power number ($=Pg_c/\rho n^3 d^5$) $[-]$

Re=Reynolds number ($=\rho nd^2/\mu$) (for mixing)

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

subscripts

b=Bulk temperature

w=Wall temperature

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