DEVELOPMENT OF MODIFIED FT (MFT) PROCESS

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ABSTRACT

Two-Stage Modified FT(MFT) process has been developed for producing high-octane gasoline from coal-based syngas. The main R & D are focused on the development of catalysts and technologieal process. Duration tests were finished in the single-tube reactor, pilot plant (100T/Y), and industrial demonstration plant (2000T/Y). A series of satisfactory results has been obtained in terms of operating reliability of equipments, performance of catalysts, purification of coal-based syngas, optimum operating conditions, properties of gasoline and economics etc. Further scaling-up commercial plant is being considered.

INTRODUCTION

China has abundant resource of coal, but that of oil and natural gas is insufficient in comparison with the large populetion. The coal production has been growing rapidly in recent years. At present, over 75% of the total energy consumption in economical activities and daily life is derived from coal. Air pollution is becoming an increasingly serious problem in many urban areas. On the other hand, in some regions, e. g. in Shanxi province, transpotation is the limiting factor of coal production. Growing demand for synfud and availability of cheap coal provide good opportunity for the development of synfuel technologies. It is considered as a comprehensive solution of the above problems, a urgent need and also of long term singnificance.

Fischer-Tropsch Synthesis (FTS) is one of the most important way to produce liquid fuel from syngas, which was already commercialized in South Africa (SASOL). However, the composition of product in FTS is very complicated, and the fraction of gasoline with unsatisfactory quality in product is limited.

China had experience in FTS. In the 50's, an intensive R&D of FTS were finished. Unfortunately, the programme was interrupted after pilot scale tests because of rapid growth of petroleum production in China.

Since 1980, the catalysts and process research on FTS was resumed in many institutes and Universities. Based on the above studies, ICC,CAS (Institute of Coal Chemistry, Chinese Academy of Sciences) has succeeded in combining FTS catalyst and zeolite catalyst into an integrated two-stage process for producing high-octane gasoline, i. e. Modified FT Synthesis (MFT) process, which has been approved and being funded by the chinese government as state key projects during the 7th and 8th five-year plan. This report has briefly summarized the major results of R & D in MFT process.

MODIFIED FT (MFT) PROCESS

I . FT Synthesis

It is well known that in the conventional FTS the performance of gasoline obtained were not good on quality and quantity. Table 1 illustrated the typical product composition of conventional FTS, Which has the disadvantages :

* Very complicated product distribution. (mainly $C_1 \sim C_{50}$)
* Low gasoline fraction. (<40%)
* Poor quality of gasoline (octane No. <70)
* Miscellaneous & complicated upgrading process of product.
* Only suitable to large scale commercialization.

II . Development of MFT Process

In order to overcome these shortages, we have successfully developed a two-stage Modified FT Synthesis (MFT) process for producing high-octane gasoline with high yield, which showed much better performance than any other one- stage hydrocarbon synthesis from syngas.

1. Principle and Procedure

Figure 1 showed a simplified block flow diagram of MFT process. The purified coal-based syngas is first passed through the 1st-Stage reactor (single-or multi-tube fixed bed) containing Fe-based catalysts for convertional FTS, and then the product effluents therefrom seperated the wax fraction flows into the 2nd-Stage reactor (adiabatic fixed bed) filled with a zeolite catalyst, where a number of reactions, such as cracking, isomerization, cyclization, aromatization and conversion of oxygenates to hydrocarbons etc, take place. The product hydrocarbons coming out of the 2nd-reactor is enrichened with gasoline fraction. The tail-gas, a part of which is recycled, can be used for town-gas. The aqueous phase product was drained off without environmental pollution treatment.

Since the exothermic heat of 1st - stage FTS is so considerable, a high velocity fixed bed operated with tail - gas recycle was used to remove the large heat of reaction and to redistribute the temperature along the catalyst bed smoothly.

2. Technological Features

The major features of MFT process are as follows:

— Distribution of product hydrocarons ($C_1 \sim C_{50}$) can be highly confined to gasoline fraction ($C_5 \sim C_{11} > 70\%$) with higher yield

— The high - octane gasoline can be used as motor fuel satisfactorilly.

— It is simple and easy to operate at mild conditions.

— The product can be adjusted into different available fractions, such as gasoline, hard wax and towngas.

— It is suitable to small or middle scale commercialization.

DEVELOPMENT OF CATALYSTS

I. Fe - based Catalyst(1st-stage)

In the early studies, a spherical fused - Fe catalyst with higher activity was developed for the 1st-stage use and run over 1000 hrs both in lab and industrial size single tube fixed bed reactor. The fused - Fe catalyst can be easily prepared and more applicable to fluidized bed reactor.

Comparing with the fused catalyst, the precipitated - Fe catalyst shows higher activity and better stability. Furthermore, it can be directly pretreated with syngas at mild conditions, which led the catalyst to have a potential advantage for commercial use. Table 2 summerized the performance of Fused - and Precipitated - Fe Catalyst in MFT process.

I. Zeolite catalysts (2nd - Stage)

Several types of zeolites have been synthesized for the 2nd-stage in both bench scale (5L, 100L) and industrial size ($1M^3$) autoclaves. The structure and properties were also characterized as shown in Table 3.

OPERATION AND RESULTS OF MFT PROCESS

A series of test units has been used for R & D of MFT process. Many sets of 5 - 10ml fixed bed microreactor, gradientless reactor, 100 - 200ml model units, and 2 - 5L single tube reactors were used for catalyst evaluation, kinetics, process development and reactor engineering etc. We also constructed a pilot the comparing results of pilot and industrial demonstration plant in detail.

INDUSTRIAL DEMONSTRATION PLANT

The industrial demonstration plant(2000T/Y) was constructed in 1993 at a small synthetic ammonia plant and being in operation for in 1994 more than 1700 hrs to demonstate the performance at commercial operating conditions.

As expested, the performance of demonstration plant was very satisfactory, and no siginficant scale-up effects have been observed. Product selectivity, gasoline yield, and quality are similar to those of the bench unit and pilot plant. The gasoline with octane number more than 90 contains no detectable impurities such as sulfur, nitrogen, oxygenates etc. It has passed quality screencing and in-vehicle tests and given satisfactory performance as commercial gasoline. Table 6—9 summerized the data for demonstration plant.

I . Syngas(water gas)

1. Production

The syngas was supplied by the ammonia plant, where water gas was procuced by a moving bed gasifier using anthracitic coal. This gasifier is manufactured in China at low cost, and workers are familiar with this technology.

2. Clean up

A major cost when using coal raw material for syngas generation is the need to remove sulfur and other poisons. The AMISOL Process (Absorption of Alcohol-Amine Solvent) was used to remove the H_2S, COS, CS_2 and CO_2 etc. A home made deoxidizer was used for removing the trace amount of oxygen in syngas. The residual total sulfur compounds is less than $1mg/NM^3$ syngas, while the oxygen content can be less than 10ppm, which satisfied the limit of catalysts.

I . Pretreatment of Precipitated—Fe catalyst

The precipited-Fe catalyst was pretreated with syngas at mild conditions. From characteristics and performance of catalyst, it can be found that direct pretreatment with syngas was simple and beneficial to the formation of iron carbides, which led the catalyst to have higher activity and good stability. In prospect, the catalyst will have a potential advantage for comercialization.

I . Effects of Technological Parameters on Catalyst Performance

1. The Effect of Temperature on Catalyst Performance

Fig. 2. shows the temperature effect on catalyst performance. It indicated that the CO conversion increases significantly with increasing temperature.

2. The Effect of Syngas Space Velocity on Catalyst Performance

Results of space velocity traverse are shown in Fig. 3. As shown in Figure, the CO conversion and yield of liquid fuel fall with increasing space velocity, However, the Space-Time-yield (STY) of fuel increases at the first and then fall down with increasing space velocity and a maximum value could be found at $GHSV=500hr^{-1}$.

3. The Effect of Receyle Ratio of Tail-gas/Syngas on Reaction Performance

Results in Table 10 show that the fuel yield increases significantly with increasing recycle ratio of tail-gas/syngas due to the increment of H_2 conversion and usage ratio of H_2/CO. The results implied that the recycle of tail-gas restrains the Water-Gas Shift Reaction and results in effective use of syngas.

Ⅳ. Kinetics & Reactor Design

1. Kinetics

For process design and reactor scale-up, kinetics of FTS on two types of precipitated catalysts were tested in an internally recycled gradientless reactor in the induserial operation ranges. For two types of catalysts (Fe/Cu/K, Fe/Mn/K), the following rate expression gave the best fit, i. e.

$$-R_{(H_2+CO)}=kP_{H_2}P_{CO}/(P_{CO}+bP_{H_2O})$$

Where the k is the kinetic constant and b is a function of temperature, i. e. $k=k_0\exp(-E/RT)$, $b=b_0\exp(-\Delta H/RT)$, $E=50-70Kj/mol$, $\Delta H=55-75Kj/mol$. The apparent activation energy of indicated that the internal diffusion is probably existent for the catalysts. While the value of ΔH implied that water is more strongly adsorbed on the catalyst surface than that of CO.

The kinetics of the Water-Gas-Shift reactron was also investigated. The models were obtained as fallows and the activation energy was ~120kJ/mol.

$$R_{CO_2}=K_W(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}/K_{eq})/(P_{H_2O}P_{CO}+bP_{H_2O})$$

2. Reactor Model and Tests Verify

By using one and two-dimensional pseudo-homogeneous reactor mathematical models, effects of operating conditions on the temperature profiles and CO conversions were investigated intensively. The mathematical model was also used to predict the performance of different commercial reactor designs.

- **Axial Temperature Profile**

Figures 4—6 describe the axial temperature distributions along the catalyst bed for the simulation of pilot plant and industrial demonstration reactor. As can be seen from the figures, calculations results showed good agreement with these obtained insite with a maximum mean error of 4℃. However, the data for one-dimensimal model is somewhat higher than that of two-dimensional model due to the negelet of radial transfer resistance.

• **Radial Temperature Profile**

The radial temperature profiles for simulating of single-tube, pilot plant and demonstration reactors are shown in Figure 7. The curves calculated from the two-dimensional model indicated that radial temperature difference for three scale reactors are all less than 7℃. However, the case for industrial reactor is somewhat higher than the others, which expected as scaling-up.

• **CO Conversion**

Effects of operating variables on CO conversions were also studied. Briefly, the CO conversion increases significantly with the temperature rise. As can be seen from Figure 8, the CO conversions for three scale reactors were all increased straightly along the catalyst beds. This trend in CO conversions implied that the temperature distribution for the entirebed is uniform, and thus, the reactor could be operated smoothly. Furthermore, the calculated conversions are very closed to the measured data with a maximum error of 15%.

V. **Summerized Points**

The results of pilot and demonstration plant may be summarized:

— The experimental equipments of plant are simple, good operation, easy control, and no significant scale-up effects have been observed.

— The higher velocity fixed bed and good heat transfer may form a uniform temperature profile in 1st-stage multi-tube reactor.

— The performance of catalysts for two stages, in terms of activity, selectivety, strength and regeneration etc. are rather convincing.

— The gasoline product with Octane Number of more than 90 is unleaded and chemically similar to gasoline made from crude oil.

— The purification of coal-based syngas (residual total sulphur componds: $<$ 1mg/Nm^3, O_2: $<$10ppm) was satisfactory for the catalysts.

ECONOMICS

I. **Economical Analysis for Demonstration Plant**

Based on the data of demonstration plant, a economical analysis is summerized in Table 11. As shown in the table considering the lower price of gasoline in China, the Fuel-Wax-Towngas joint production will be a good economic option.

II. **Economical Projection for Commercial Plant**

According to the situation of China, combining to the gasoline and FT wax market predictions, a commerical plant of MFT should be chosen to reconstruct gasoline in China, the Fuel-Wax-Towngas joint production will be a good economic option.

I. Economical Projection for Commercial Plant

According to the situation of China, combining to the gasoline and FT wax market predictions, a commerical plant of MFT should be chosen to reconstruct an operating towngas plant or ammonia plant with available coal gasification and purification systems. A brief economcal projection for the first case is shown as Table 12.

CONCLUDING REMARKS

Energy is the most important issue facing modern China. Shortage in erergy supply is one of the limiting factors of economical growth at present. Since China is a developing country, the technologies appropriate to China should be

- Suitable for chinese coal with wider range.
- Affordable for smaller enterprises
- Simple process and easy operable

The MFT technology developed by ICC, CAS is one of the more efficient process for the purpose, which has been reached the stage of industrial demonstration plant. A scaling-up commercial plant is beeing considered at present.

In the meantime, attempts are being made to explore the international cooperation on the coal conversion technology, especially for MFT process. Furthemore, a pilot plant base was constructed for scaling-up new coal conversion processes. The base is open to other organizations at home and abroad. We believe that international academic exchange programme will be helpful for the development of clean coal technology in China as well as in the world.

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Table 1. Typical Product Compositions of Conventional FT Synthesis (SASOL)

Process Features	Fixed-Bed (ARGE)	Fluidized-Bed (SYNTHOL)
HC Distribution (%)		
Methane	5	10
LPG (C_2-C_4)	13	33
Gasoline (C_5-C_{12})	22	39
diesel (C_{13}-C_{19})	15	5
Wax (C_{20}^+	41	6
Oxygenated compounds	4	7

Table 2. A comparison results of Fused and Pptd-Fe in MFT process

Catalysts	Pptd-Fe/Zeolite			Fused-Fe/Zeolite		
Reaction Temp. (℃)*	235/300	230-233/300	260-265/320	250/310	260/320	275/300
H_2/CO (feed)	2	2	1.3-1.4**	2	2	1.5-1.7**
Recycle ratio (R)	0	3.4	3.0	0	3.5	3
CO conv. (%)	92.4	88	84.6	90	85.0	70
Usage ratio (H_2/CO)	0.97	1.6	1.26	0.7	1.7	1.4
HC Distribution (%)						
CH_4	7.19	4-4.5	7.26	9-16	14.0	10
C_2	2.9	0.7	1.66	7-10	8.5	6
C_3-C_4	14.4	16	9.53	10-15	22.5	24.0
C_5^+	75.5	72-80	81.54	60-74	55.0	60

Table 3. Physico-Chemical Characteristics of Zeolites

SiO_2/Al_2O_3	60-70
Na_2O (%)	0.1-0.5
Surface Area (M^2/g)	400-500
Pore Capacity (CC/g)	0.18-0.21
Adsorbed Amount (%)	
N-hexane	10-14
Cyclo-hexane	5-8
H_2O	7-9

Table 4. Major Results for Different Scake of MFT

1st-reactor Catalyst volume(V_1)	Fixed bed 10ml	Recyde fixed 200ml	Recycle fixed 5L	Pilot multi—tubes 0.3M^3	Demonstration Multi-tubes 7.2M^3
Time-on-stream (hr)	7560	>500	>500	>1500	>1000
P(MPa)	2.5	2.5	2.5	2.5	2.5
GHSV(hr^{-1})	500	510	500	350—450	400—520
T,(T_1/T_2℃)	250—270/300	255/300	260—265/295	265/300	265—270/310—330
H_2/CO (feed)	2*	2*	1.3—1.5**	1.3—1.5**	~1.5**
Recycle Ratio	0	~3.5	3.0	3.0	3.0~3.5
CO conv. %	75—80	86	85	81	70—79
HC distribution(wt%)					
CH_4	12—15	10—12	10—12	13—15	10—13
C_2	2—5	3—4	2—5	4—6	3—4
C_{3-4}	17—20	18—20	17—19	15—20	24—28
C_5^+	60—65	64—70	64—71	59—68	55—63

* Syngas: ($CO+H_2$)≥95% prepared by cracking of Methanol,

* * Coal-based Syngas(watergas):($CO+H_2$)≥85%

Table 5. Major Specifications and Results of MFT Pilot and Demonstration Plant

Plant	Pilot	Demonstration
Feed rate of syngas (M^3/hr)	150	3,600
Capacity of gasoline (T/Y)	100	2,000
1st-Stage Synthesis Reactor		
Reactor type	Multi-tube	Multi-tube
Reactor size	Φ26×4,000mm×155	Φ32×7,000mm×1320
Catalyst volume (m^3)	0.3	7.2
2nd-Stage Reforming Reactor		
Reactor type	Adiabatic	Adiabatic
Reactor size	Φ420×3,740mm	Φ1,600×12,500mm
Catalyst volume (m^3)	0.538	10.8
Time—on—stream(hrs)	1549	956
Operating Conditions		
Temp. 1st-stage (℃)	250-260	260-270
2nd-stage (℃)	310-330	330-350
Pressure (Two Stage) (Mpa)	2.5	2.5
GHSV (Hr^{-1})	400	~500
H_2/CO (Feed*)	1.44	1.5
Recycle Ratio	3-4	3
CO Conversion (%)	82.1	72
H_2/CO Usage Ratio	1.31	1.31
HC Distribution (Wt%)		
C_1	6.20	12.63
C_2	3.84	3.17
C_{3-4}	17.78	21.54
C_5^+	72.12	62.66

* Coal-based syngas (water gas): $(CO+H_2)\% \approx 85\%$

Table 6. Properties of Gasoline of MFT Demonstration Plant

№	1		2	
1. group composition(%)	100.0		100.00	
Aromatics	40.35		40.26	
N-paraffins	10.12		9.96	
Iso-paraffins	34.21		34.65	
Cyclo-paraffins	10.17		9.07	
Oleffins	1.15		1.91	
Unknown	4.00		4.16	
2. Carbon Number Distribution(%)	100.00		100.00	
~C_5	18.12		19.31	
C_6	19.77		19.98	
C_7	24.51		25.54	
C_8	25.42		24.71	
C_9	8.84		7.38	
C_{10}	2.73		2.19	
C_{11}	0.18		0.15	
$\geqslant C_{12}$	0.43		0.74	
3. Aromatics composition(%)				
C_6(benzene)	3.20		4.22	
C_7(xylene)	30.09		33.93	
C_8	46.34		45.23	
C_9	15.39		12.92	
C_{10} durene	0.52	4.88	0.45	3.60
C_{10} the others	4.36		3.15	
C_{11}	0.09		0.1	

Table 7. Composition of Aqueous Phase Product of MFT Demonstration Plant

composition(%)	1	2	3
Methanol	0.0021	0.0663	0.0120
Ethanol	0.0183	0.0105	0.0204
N-propanol	0.0019	—	0.0002
$\sum^*$	0.0324	0.0928	0.0475

* The others are H_2O

Table 8. Typical Composition of Syn—gas and Tail—gas of MFT Demonstration Plant

Gas	H_2	CO	N_2	CO_2	CH_4	C_2°	C_3°	C_4°	C_{5-6}°	H_2/CO	$CO+H_2$(%)
feed	52.72	34.72	11.06	0.2	1.30	—	—	—	—	1.52	87.44
Tail	44.11	15.76	10.10	14.2	10.27	0.96	2.16	1.69	0.75	2.79	59.87

Table 9. Propeties of FT Wax Produced from MFT Demostration Plant

Sample	Demonstr. Plant FT wax	Sasol FT wax(H_1)	Rubrchemie FT wax(hard)
Colour	White	White	White
Hardness	hard	hard	hard
Penetrometer number(25℃)	<5	<1	4.0
Drop point(℃)	111℃±1	—	99
Setting point(℃)	100℃±1	>94.5	90
Soluble acid and alkali	no	—	—
Acid number	—	<0.1	<0.1

Table 10. The Effect of Recycle Ratio of Tail—gas/Feed—gas on Reaction Performance

Recycle ratio(R)	0.31	3.0
CO conv. (%)	73.55	74.78
H_2 conv. (%)	52.72	62.7
C_3^+ g/NM^3($CO+H_2$)	59.0	90.7
Usage ratio H_2/CO	1.13	1.35

Table 11. Economic Analysis for Demonstration Plant

			Full-Towngas joint production		Fuel-Wax-Towngas Joint production
• Basis:					
Input:	Coal	(Ton/Y)		10000	
	Electricity	(KWH/Ton)		4426	
	Steam	(Ton/hr)		1	
	Water	(Ton/hr)		90	
output:	Gasoline	(Ton/Y)	1940		1261
	Wax	(Ton/Y)	—		700
	Residum	(Ton/Y)	60		39
	Town gas	(NM_3/Y)	1111×10^4		1111×10^4
• Capital investment		(RMB*)		25million	
• capital	Costs				
	Gasoline	(RMB/Ton)		2415	
	Wax	(RMB/Ton)		13600	
	Residuum	(RMB/Ton)		800	
	Town gas	(RMB/NM^3)		0.60	
• Total output value		(RMB/Y)	784×10^4		1571×10^4
• After-Tax profit		(RMB/Y)	62.4×10^4		529×10^4

Table 12. Economic Projection for Commercial Plant*

Input:	Syngas	60,535NM^3/hr
Output:	gasoline	18640T/Y
	wax	10543T/Y
	Towngas	17448NM^3/hr
	Residiuum	983T/T
Total investment		1.0 Billion RMB
Revenue		0.98 Billion RMB
After-Tax profit		0.406 Billion RMB
Payout		4.7 year

* Based on the Reconstruction of a Operating Towngas Plant

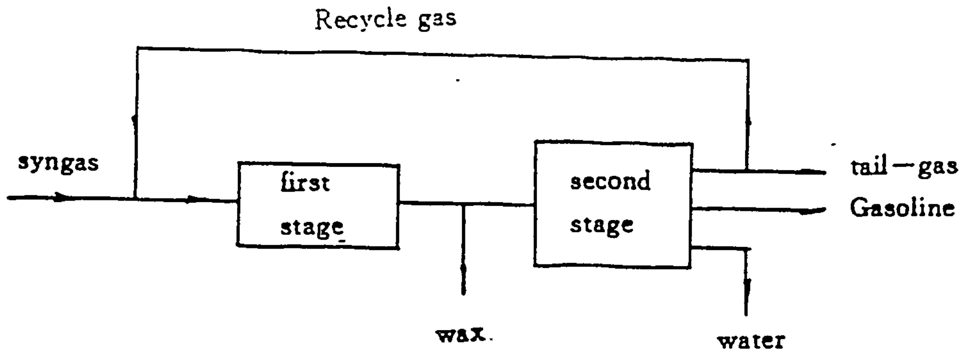


Fig. 1. Simplified Block Flow Diagram of MFT process

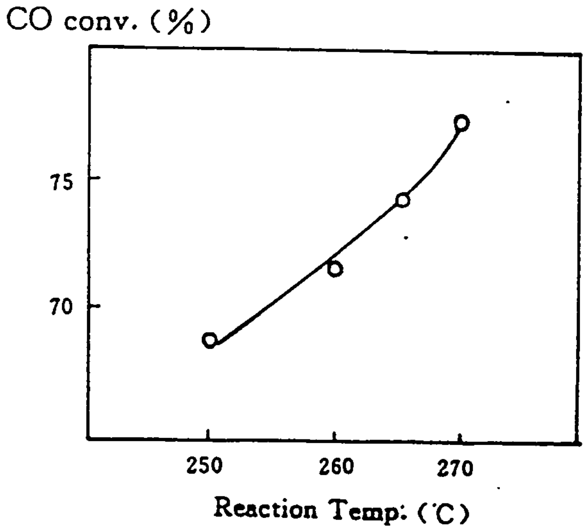


Fig. 2. The effect of reaction temprature on catalyst performance

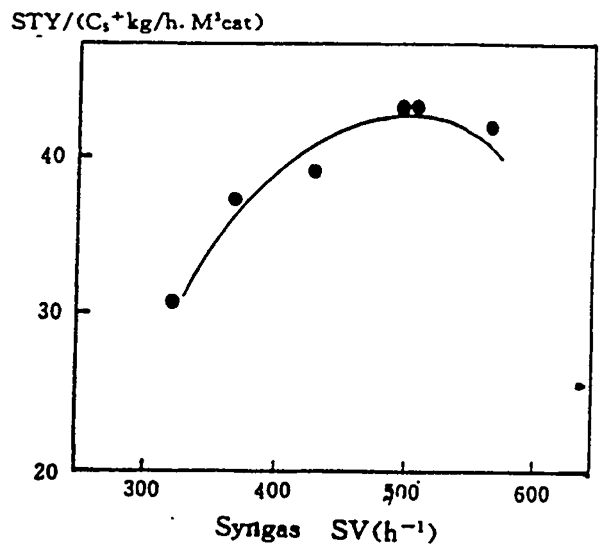
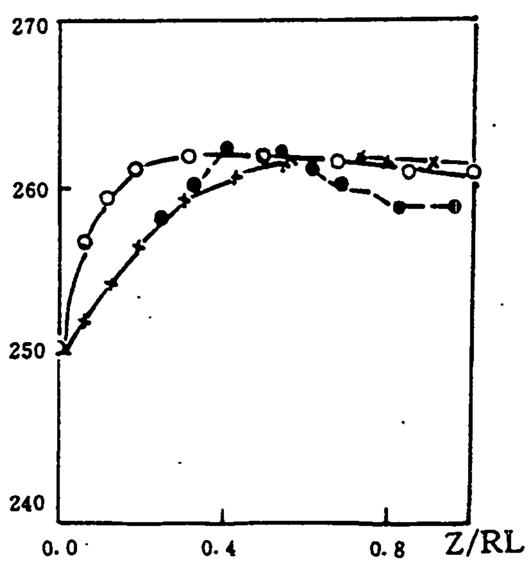


Fig. 3. The effect of Syngas space velocity on reaction results



$D_t = 32mm, R_l = 7.0m, SV = 500hr^{-1}, T_0 = 250℃, T_w = 255℃, R_N = 3.0$
○ Data from one-dimensionol model
× Data from two-dimensionol model
● Data measured insite

Fig. 4. Axial temperature profile for single-tube Simulation

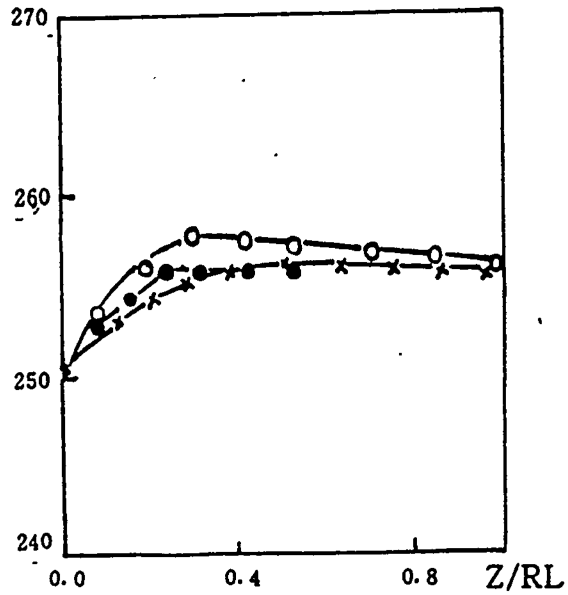


Fig. 5. Axial temperature profile for pilot plant $D_t=26mm, R_L=4.0m, SV=425hr^{-1}, T_0=T_w=250℃$, $R_N=3.5$, others see figure 4.

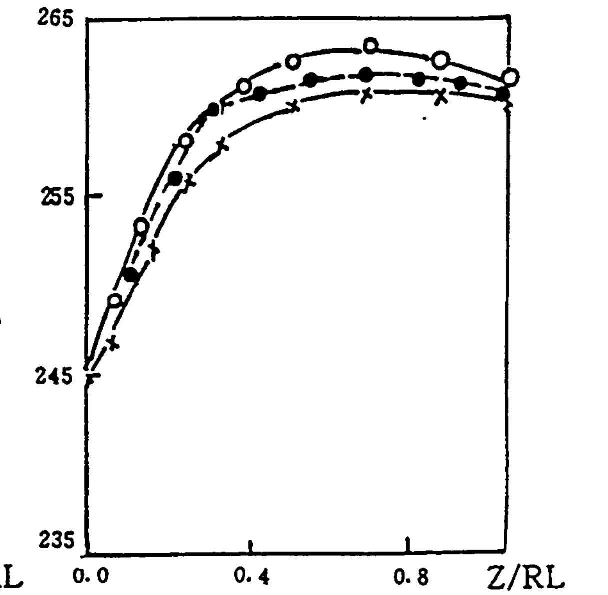


Fig. 6. Axial temperature profile for industrial reactor $D_t=32mm, R_L=7.0m, SV=324hr^{-1}, T_0=T_w=245℃$, $R_N=3.3$. others see figure 4.

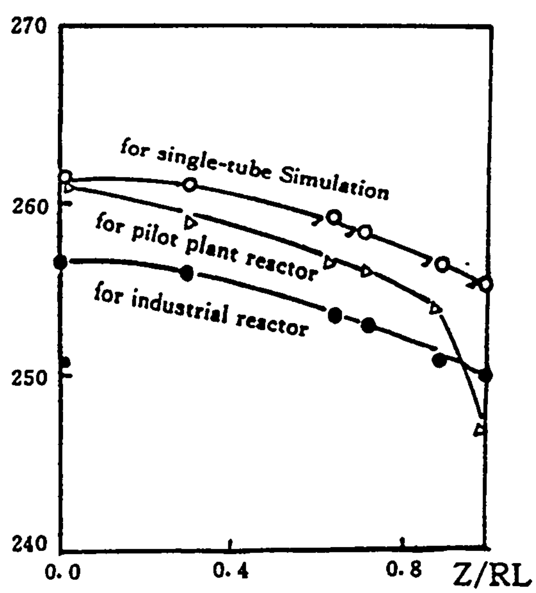


Figure 7 Radial temperature profile

operation voriables see figure 4-6.

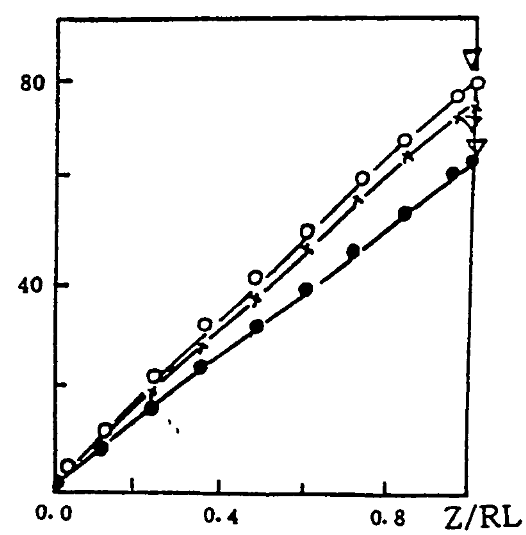


Figure 8 CO conversions along the catalyst bed

× Pilot plant

○ Industrial demonstration plant

△ measured data

Operation condition can see figures 4 to 6