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Economics of Polysilicon Process-A view from Japan

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Abstract

Osaka Titanium Co., Ltd. and Shin-etsu Chemical Co., Ltd. have researched the production process of solar-grade Silicon (SOG-Si) through trichlorosilane (TCS) in a program sponsored by New Energy Development Organization (NEDO). The NEDO process consists of the following two steps:

(1) TCS production from by-product silicon tetrachloride (STC)
(2) SOG-Si formation from TCS using a fluidized-bed reactor (FBR)

Based on the data obtained during the research program, the manufacturing cost of the NEDO process and other polysilicon manufacturing processes listed below were compared.

(1) TCS processes; Conventional Siemens, NEDO FBR and Recycle-filament processes
(2) Dichlorosilane (DCS) process; Hemlock filament process
(3) Monosilane (MS) processes; UCC filament and UCC-JPL FBR processes.

The manufacturing cost was calculated on the basis of 1000 tons/year production, using data and information in reports issued by the Subcommittee on Silicon Metal and Resources, Japan Electronic Industry Development Association ("the Subcommittee Reports") and in other data in published reports, magazines, newspapers, etc.

Actual manufacturing costs are difficult to compare because of differences in local conditions, production scale, contents of direct and indirect costs and reliability of published data. To reduce these differences, the published data was modified according to a certain estimate method prior to manufacturing cost calculation.

Our cost estimate showed that the cost of producing silicon by all of new processes is less than the cost by the conventional Siemens process. Using a new process, the cost of producing semiconductor-grade silicon (SEG-Si) was found to be virtually the same with any of the TCS, DCS and MS processes when by-products are recycled.

The SOG-Si manufacturing processes using FBR, (the NEDO and UCC-JPL FBR processes,) which need further development for practical application, have a greater probability of cost reduction than the filament processes.

1. INTRODUCTION

Research and development of various processes for manufacturing low cost SOG-Si are under way worldwide. One approach is the solid purification process, in which SOG-Si is produced directly from the reduction of silica in solid state. A substantial cost reduction can be expected, but the impurity removal technique has not yet been established. In this process it would be difficult to upgrade the present SOG-Si to SEG-Si in the future. Another approach to cost reduction uses gas purification based on the current SEG-Si manufacturing process. This refinement of the gaseous silicon compounds satisfies the quality required for as SOG-Si.

This report compares manufacturing costs of gas purification processes whose developments are reaching completion.

Sponsored by NEDO, the Japan Electronic Industry Development Association investigated demand, processing technologies, and future tasks regarding silica, metallurgical silicon (MG-Si) and polysilicon, necessary for solar cell manufacture. The summary of this investigation was reported in the Journal of Electronics Industry (1). Manufacturing cost were estimated on the basis of the data in the Subcommittee Reports and the final reports of Hemlock and UCC (2, 3) as well as data published in newspapers, magazines, etc.

2. MANUFACTURING PROCESSES AND MATERIAL FLOW

2-1. TCS: Conventional Siemens Process

In this most common SEG-Si manufacturing process, polysilicon deposits from TCS onto silicon slim rods (filaments) in a bell jar reactor. Figs. 1 and 2 show the process diagram and the material flow of this process (2).

HCl is produced via a H_2-Cl_2 reaction; additional H_2 is used to ensure 100% Cl_2 consumption in the reaction. Passing through absorption, stripper and drying towers, HCl is introduced into MG-Si FBR at around 300°C to produce TCS. A reaction gas roughly of 90 % TCS and 10 % STC is cooled and condensed. Impurities such as B, P and carbon compounds are removed by distillation. A purity of around 11 N is required to obtain the material gas for SEG-Si. Distillation columns are designed to be operated with a high reflux ratio and equipped with many trays. This process requires a large amount of energy per unit weight of product.

Polysilicon deposits on silicon filaments heated to 1050 - 1150°C. The conversion yield of TCS into silicon is as low as 10 to 20 %. Unreacted TCS and by-product STC in decomposition reactor are then cooled, condensed, collected and distilled. The distilled TCS is reused as materials, whereas STC is removed from the process and used as raw material for silica powder, etc. The major problems of this conventional Siemens process are; 1) the amount of by-product STC over ten times or more than that of polysilicon, and 2) a large amount of energy required for unit weight of product.

2-2. TCS: NEDO Process

This process in which MG-Si is converted into SOG-Si by supplying energy only, ideally requires no other raw material than MG-Si. The process diagram and material flow are shown in Figs. 3 and 4.

Distillated TCS is diluted with H_2 and introduced to a FBR filled with silicon seeds. SOG-Si deposits on the seeds, growing into larger granules. As in the conventional Siemens process, unreacted TCS and by-product STC are condensed and recovered. After distillation, TCS then being reused as material, and by-product STC is used as raw material of TCS in the recycle system.

The TCS reproduction process is the same as that used in Hemlock and UCC processes, i.e.,

$$Si + 3SiCl_4 + 2H_2 \longrightarrow 4SiHCl_3$$

In the NEDO process, the reaction takes place at a lower-pressure and higher H_2/STC molar ratio than in the Hemlock and UCC processes. The relative advantages as compared with high-pressure, low-molar ratio operation depend on the equipment and operation costs required for safety and legal regulations.

A pilot plant of 10 tons/year of silicon granules has already been operated for 2000 to 3000 hours, resulting in a power requirement of 30 kwh/Si-kg for decomposition. The basic operation technology has been established, and the quality of Si in this process has already been demonstrated. Future tasks are to develop large scale FBR and establish technology for a long-term continuous operation.

2-3. TCS Recycle-Filament Process

SEG-Si is currently produced and consumed at approx. 5000 tons a year worldwide. Considering the expected increase in the consumption of semiconductors, the demand for SEG-Si is very likely to grow steadily to 10,000 to 15,000 tons in 1990. In the conventional Siemens process, where a large amount of STC is by-produced, the recycling system of STC would be necessary in a large-scale polysilicon plant.

A process, which combines filament decomposition with the recycle of by-product STC, would be one of the leading processes for manufacturing SEG-Si. In this combined process, by-product STC is fed with hydrogen into MG-Si FBR, hydrogenated and recycled as TCS.

The filament reactor used for the reduction of TCS should be made of metal. A large reactor is necessary to decrease power consumption. The process diagram and material flow of this Recycle-Filament process are shown in Figs. 5 and 6.

The calculation was done on the basis of energy and material required for the reduction in the conventional Siemens process and for the hydrogenation in the NEDO process. Fig. 6 suggests that, approaching complete recycle, the required amounts of STC and hydrogen decrease, and MG-Si is converted through

TCS and STC into SEG-Si. The key points of this process are; 1) recycling of by-product STC via hydrogenation into TCS, and 2) complete recycling of vent gases generated in reduction and other stages.

2-4. DCS: Hemlock Process

The high cost of the conventional Siemens process is mostly due to high power consumption for the reduction of TCS. Hemlock used DCS instead of TCS as material, which may lead to a lower power requirement for the reduction and to higher productivity. Figs. 7 and 8 show the process diagram and material flow of the Hemlock process. This process is characterized by; 1) DCS synthesis by TCS redistribution,

$$2SiHCl_3 \rightleftharpoons SiH_2Cl_2 + SiCl_4$$

2) polysilicon formation by DCS reduction in an improved Siemens reactor, and 3) hydrogenation of by-product STC in FBR, as in the UCC process.

Conversion efficiency of DCS into Si is higher than that of TCS, therefore less amount of DCS is required. Figs. 2 and 8 show, however, nearly the same amount of TCS is necessary as in the conventional Siemens process. Nearly the same capacity is required for TCS distillation as in the conventional Siemens process, and additionally to purify DCS suitable for SEG-Si, the boron removal column or the DCS distillation columns need to be highly efficient since the boiling points of DCS ($8.2^{o}C$) and BCl_3 ($12.5^{o}C$) are quite close.

In the DCS reduction stage, the decomposition rate, yield and temperature are more favorable than in TCS. However, to prevent metal fog generation (i.e., homogeneous decomposition), high H_2/DCS molar ratio operation is necessary, which reduces the advantage of DCS high reactivity. Another drawback is larger energy requirement for the reaction gas recovery. The energy requirement for refrigenator is larger than in TCS because of the low DCS concentration in the reaction gases and the low-boiling point materials involved in this process.

2-5. UCC-JPL FBR Process

Basic research into this process began in the early 1970's by UCC, followed by DOE-supported development (3).

$$Si + 3SiCl_4 + 2H_2 \longrightarrow 4SiHCl_3 \quad \ldots (1)$$

$$2SiHCl_3 \rightleftharpoons SiH_2Cl_2 + SiCl_4 \quad \ldots (2)$$

$$2SiH_2Cl_2 \rightleftharpoons SiH_3Cl + SiHCl_3 \quad \ldots (3)$$

$$2SiH_3Cl \rightleftharpoons SiH_4 + SiH_2Cl_2 \quad \ldots (4)$$

TCS is synthesized by hydrogenation of STC as expressed in equation (1) above, then MS is synthesized, followed by redistribution reaction (2) through (4) above.

The UCC final report proposed decomposition of MS in a free space reactor and then producing lump SOG-Si via silicon powder consolidation or casting. UCC and JPL are now conducting research for practical application of granule Si formation using FBR. The process diagram and material flow of UCC-JPL FBR process are shown in Figs. 9 and 10.

The wide boiling-point difference between MS (b.p. $-112^{\circ}C$) and the other impurities such as B or P compounds permits easy separation of impurities from MS during the distillation. As a result, distillation is simple and energy per unit distillate costs low.

In the manufacture of Si granules from MS with FBR, product/seed weight ratio should be 100 or higher (as in the filament processes) from the viewpoint of cost. MS must be substantially diluted with H_2 to achieve higher gas flow velocity in FBR. Since decomposition temperature of MS is lower than that of TCS, the design and operating conditions of FBR are easier and simpler than those in the NEDO process.

2-6. UCC Filament Process

This section discusses a process producing polysilicon with filaments from MS synthesized. MS reduction occures at a lower temperature and at a faster rate with higher conversion yield to Si than TCS and DCS. It should be noted that MS reduction begins at $400^{\circ}C$, rapidly increasing its rate at $600^{\circ}C$ and above, and reaches the full reduction level at $800^{\circ}C$ (3). To depress decomposition in free space of reactor, its temperature is maintained low providing steep temperature gradient along distance from the filaments. It would be difficult to produce large diameter polysilicon rods in a large reactor with multiple filaments, therefore the high reactivity of MS cannot be made full use of.

3. COST COMPARISON

Since actual manufacturing cost varies with local conditions, production scale, utilization ratio, reserve funds, contents of direct and indirect costs, etc., emphasis in this report is placed on relative comparison using a fixed unit cost basis. Calculation was based on the Subcommittee Reports, with production scale fixed at 1000 tons a year and the yen-dollar exchange rate at ¥250/$.

For the conventional Siemens and NEDO processes, figures were used without modification.

3-1. Equipment Cost

To estimate equipment and construction cost, the amounts of liquids/gases processed are figured at each manufacturing stage and shown in Table 1. For the construction cost for SEG-Si manufacture, data published in newspapers and magazines are used.

(1) TCS: Recycle-Filament Process

Wacker's expansion plan data in Electronic Business News of January 1, 1985, were used for estimation.

(2) DCS: Hemlock Process

The amounts of liquids/gases in Table 1 were compared with those for the NEDO process, and the estimated capital costs in the Subcommittee Report were used.

(3) MS: UCC Filament Process

The amounts of liquids/gases processed at each manufacturing stage are shown in table 1. Equipment cost for this process is taken from an article on UCC in the Nikkei Sangyo Newspaper of February 7, 1985.

(4) MS: UCC-JPL FBR Process

Since this process has many similarities to the NEDO process, the estimated figures in the Subcomittee Reports were used.

3-2. Material Cost

The amounts of materials required for manufacturing one kg of product Si were calculated on the basis of material chemical reaction. Materials unit prices are ¥300/kg for MG-Si, ¥250/kg for STC when purchased, ¥120/kg for STC when sold, ¥100/m^3 for H_2, ¥60/kg for Cl_2 and ¥70/kg for NaOH. Material costs also include cost of Si seeds, catalyst and other gases.

3-3. Electric Power Cost

For the TCS process, 100 - 150 kwh/Si-kg was reported using the most advanced equipment (4). Based on these figures, the average value of 125 kwh/Si-kg was adopted for the Recycle-Filament process.

For the DCS process, the experimental data at Hemlock CVD reactors ranged from 90 to 130 kwh/Si-kg. However, the 60 kwh/Si-kg target was considered attainable in comparison with the TCS process. When the power for other than decomposition was added, 90 kwh/Si-kg was adopted.

In the UCC filament process, power requirements in the reduction reactor were estimated apporoximately 40 kwh/Si-kg, considering heat transfer to cooling water via thermal radiation and gas conduction, and the operation temperature in TCS and in MS decomposition being 1050 to 1150^{o}C and 700 to 1000^{o}C, respectively. For the UCC-JPL FBR process, power requirments in the reduction reactor were estimated to be approximately 10 kwh/Si-kg and the total power consumption was estimated to be 40 kwh/Si-kg.

The power cost heating the STC hydrogenation reactor was also included. The power cost for one kwh was fixed at ¥15 in Japan.

3-4. Steam and Fuel Costs

Energy for heating was calculated on the basis of the amounts of liquids/gases and shown in Table 1.

3-5. Other Operating Cost

Although other operating costs, including repair cost, vary with different manufacturing processes, the fixed values given in the Subcommittee Reports were used.

3-6. Labor Cost

SEG-Si is manufactured by the filament processes and SOG-Si by the FBR processes. Considering the characteristics of these manufacturing processes and the data from the Subcommittee Reports, a 75-worker operation was assumed for the filament processes and 50-worker operation for the FBR processes.

3-7. Other Cost

Depreciation, interest, indirect and general administrative costs were calculated by the same rule as used in the Subcommittee reports.

3-8. Results

Our calculation results are shown in Table 2 and Fig. 11. For those processes in which STC is recycled via hydrogenation into TCS, manufacturing costs are virtually the same for all filament processes regardless of material gas. The manufacturing cost of SEG-Si can be reduced to 80 % of that in the conventional Siemens process.

SOG-Si manufacturing costs by the FBR processes are almost the same, at the ¥5000/Si-kg level, about 50 % of conventional Siemens-process manufacturing cost.

This study focusing on relative comparisons under fixed conditions, the resultant estimates differ from actual manufacturing costs. According to the NEDO's interim report, SOG-Si manufacturing costs with the NEDO process will be approximately ¥4300/Si-kg at a commercialized plant.

4. CONCLUSION

The manufacturing costs for various processes were estimated on the basis of SOG-Si production research sponsored by the NEDO.

When the by-products are recycled, all processes for SEG-Si will result in similar manufacturing costs. The TCS processes with filaments will be more firmly established if electric power for polysilicon formation can be lowered. The DCS process can save silicon deposition power consumption, but entails a large amount of energy for the distillation and redistribution. Moreover, the advantage of high DCS reactivity may not be fully utilized since reduction must be kept at low DCS concentration to prevent metal fog. Whereas, in the MS process, the material gas can be produced at lower cost, but the total manufacturing cost is virtually the same as those of other processes since the advantage of high MS reactivity cannot be fully utilized for the silicon formation.

The Si-granule production by FBR cost approx. ¥5000/kg. The MS process, in particular, permits low temperature operation, compared to the TCS process, and facilitates the design and development of equipment: future advances are fully hoped for.

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4. Rare Metal News, No. 1279 (1984) (Japanese)

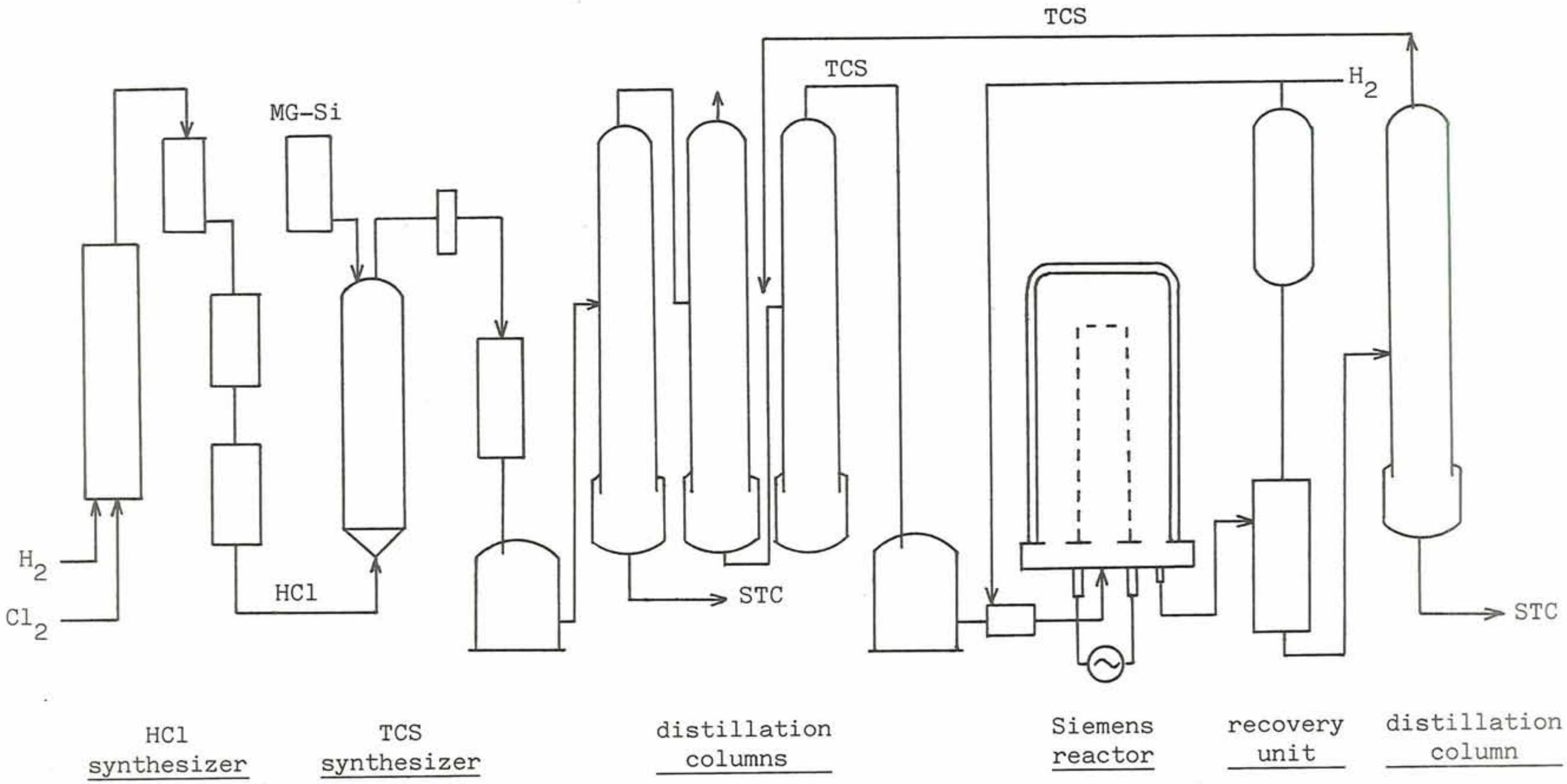


Fig. 1. Conventional Siemens Process

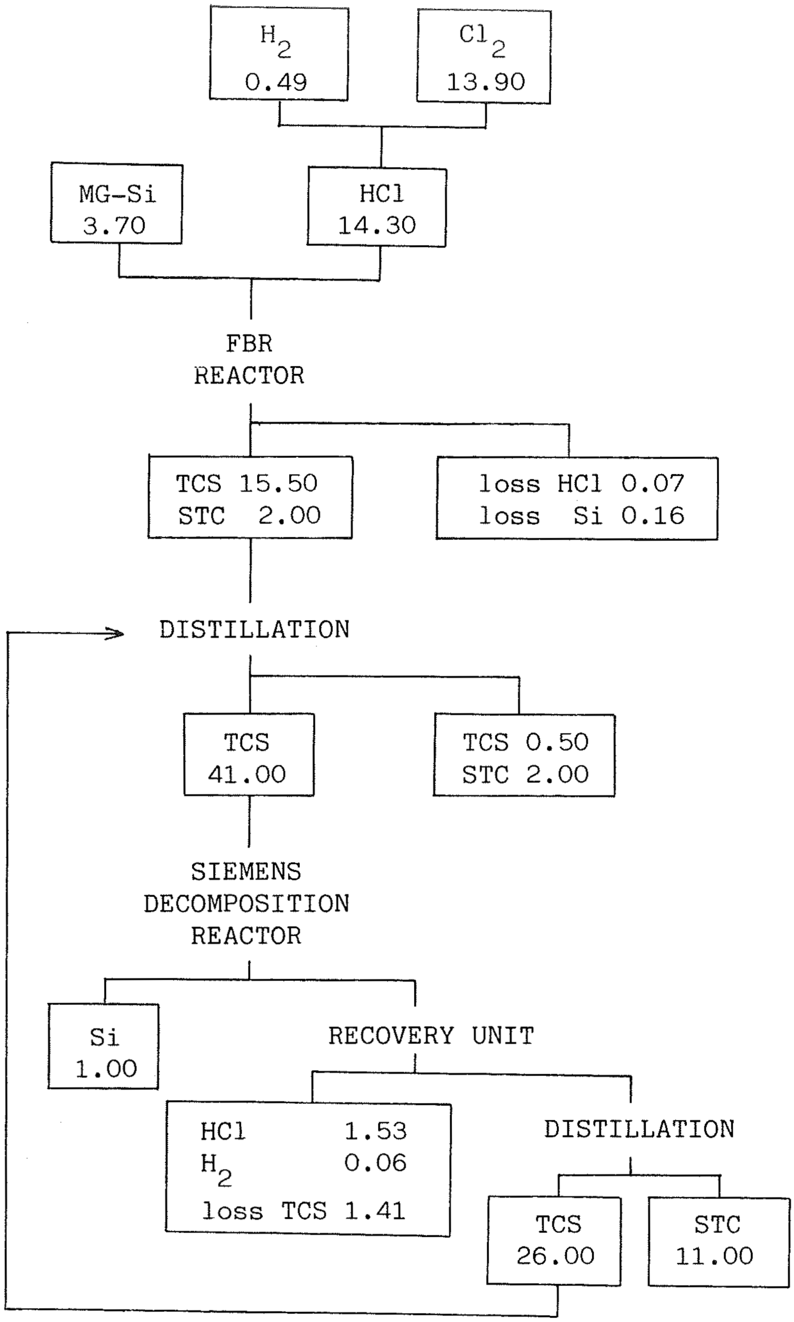
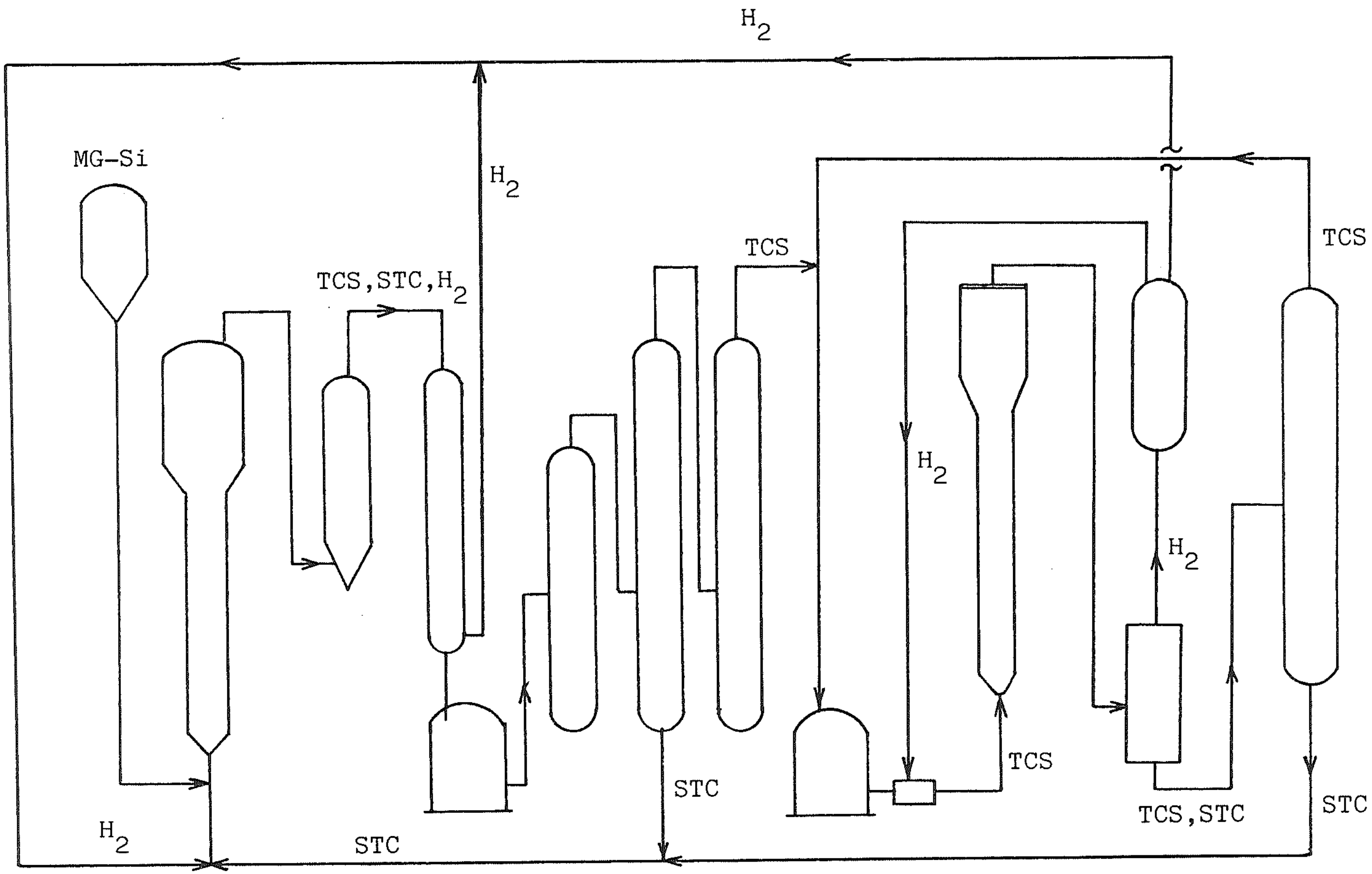


Fig. 2. Conventional Siemens Process (kg/kg-Si)



hydrogenation FBR	condenser	distillation columns	decomposition FBR	recovery unit	distillation
500–550°C 7–8 kg/cm²G	500/ 40°C 40/–15°C –15/–35°C	70/72°C 50/80°C 50/60°C	1000°C, 1 atm. H_2/TCS=60/40		

Fig. 3. TCS–Based NEDO FBR Process

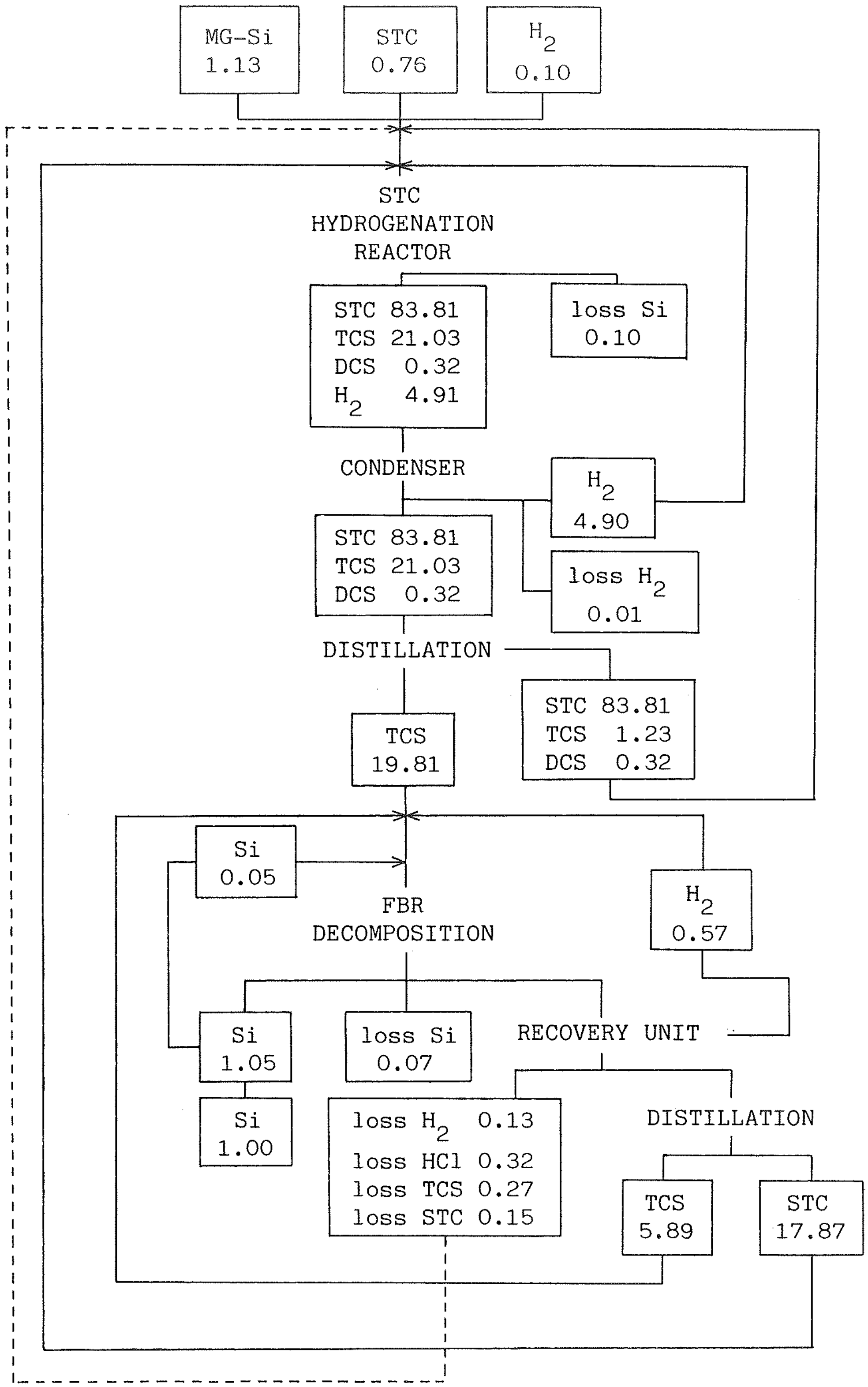
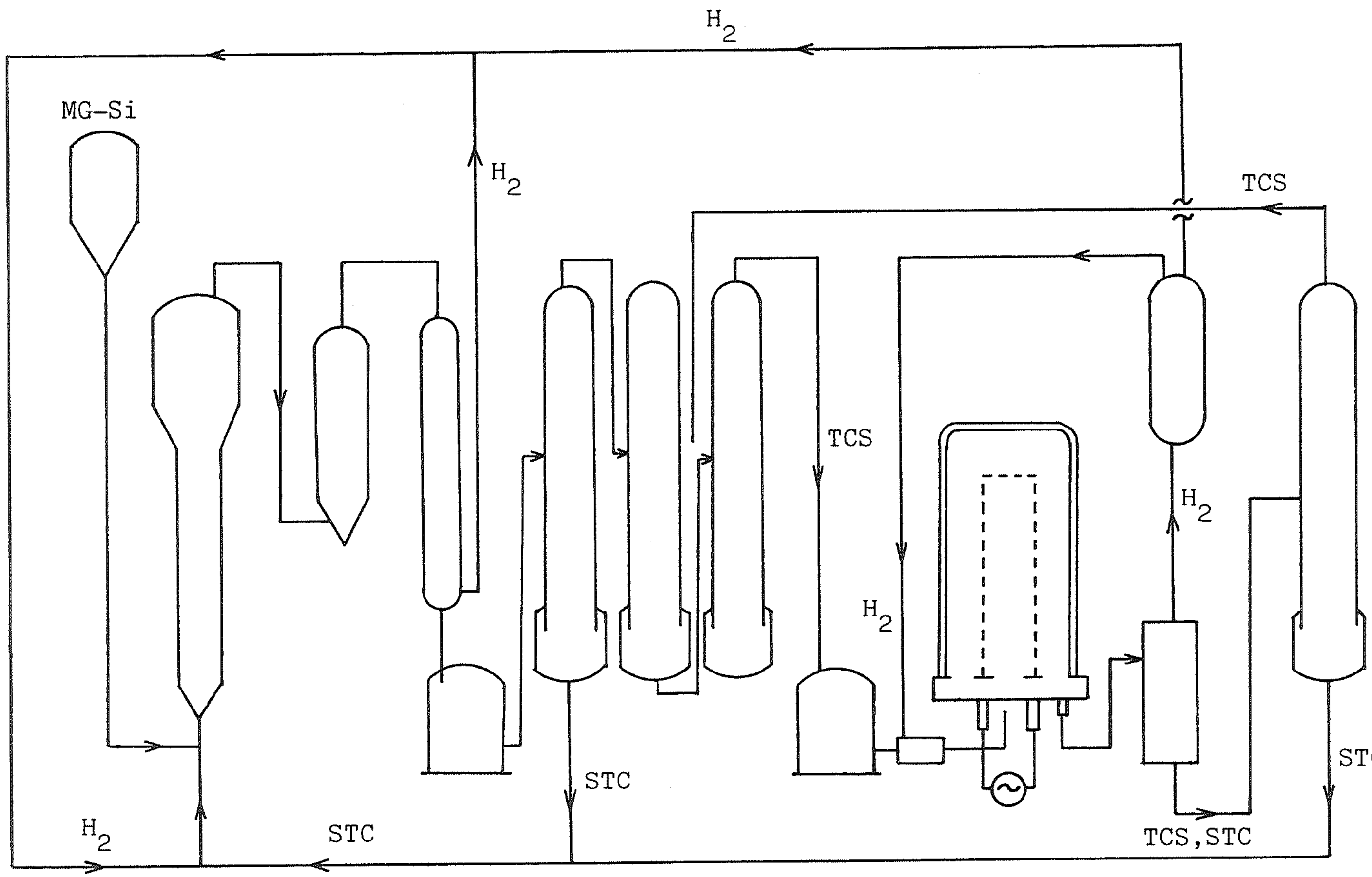


Fig. 4. TCS-Based NEDO FBR Process (kg/kg-Si)



hydrogenation FBR	condenser	distillation columns	filament reactor	recovery unit	distillation
500-550°C 7-8kg/cm^{2}G	500/ 40°C 40/-15°C -15/-35°C				

Fig. 5. TCS-Based Recycle Filament Process

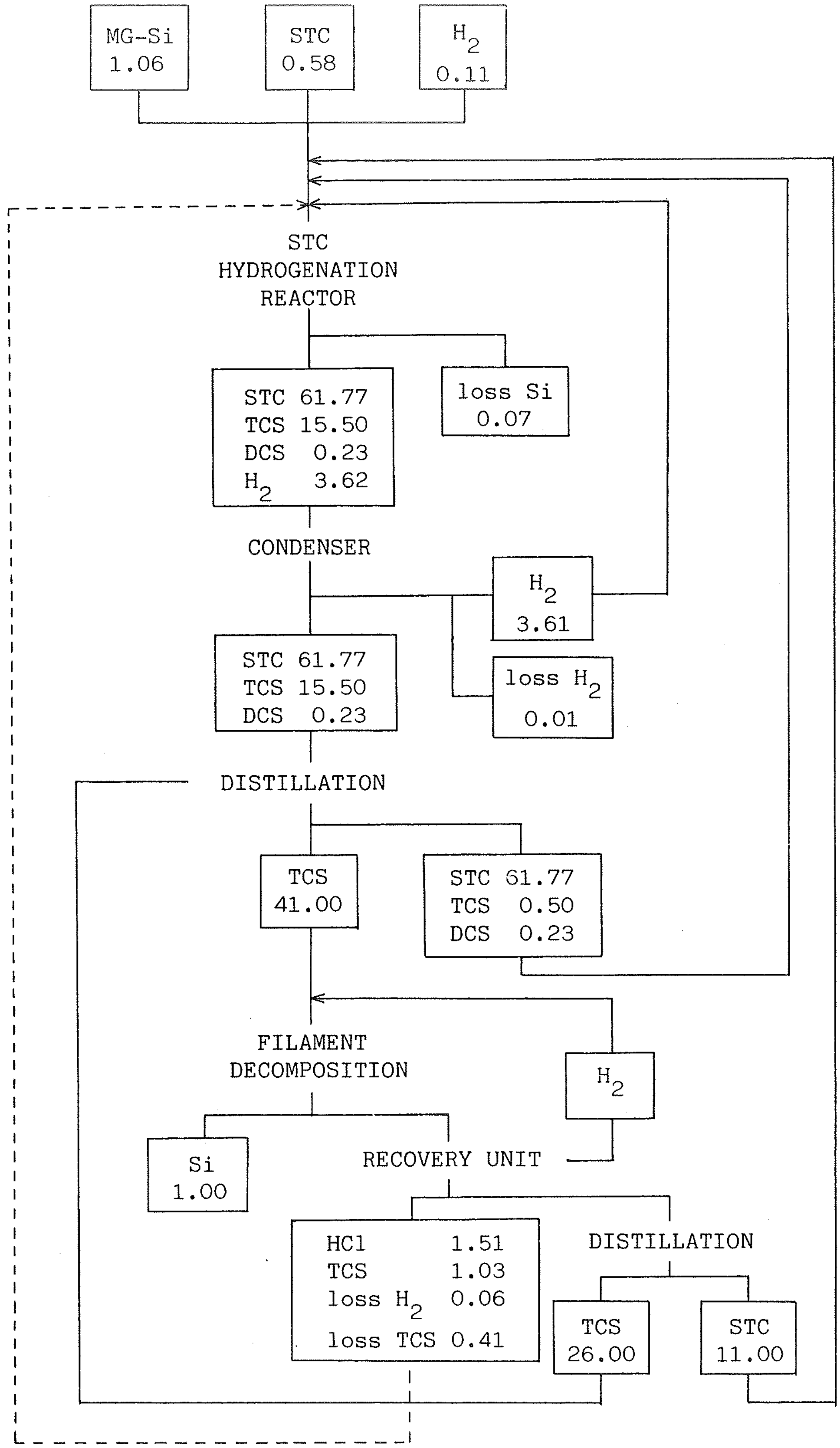


Fig. 6. TCS-Based Recycle Filament Process (kg/kg-Si)

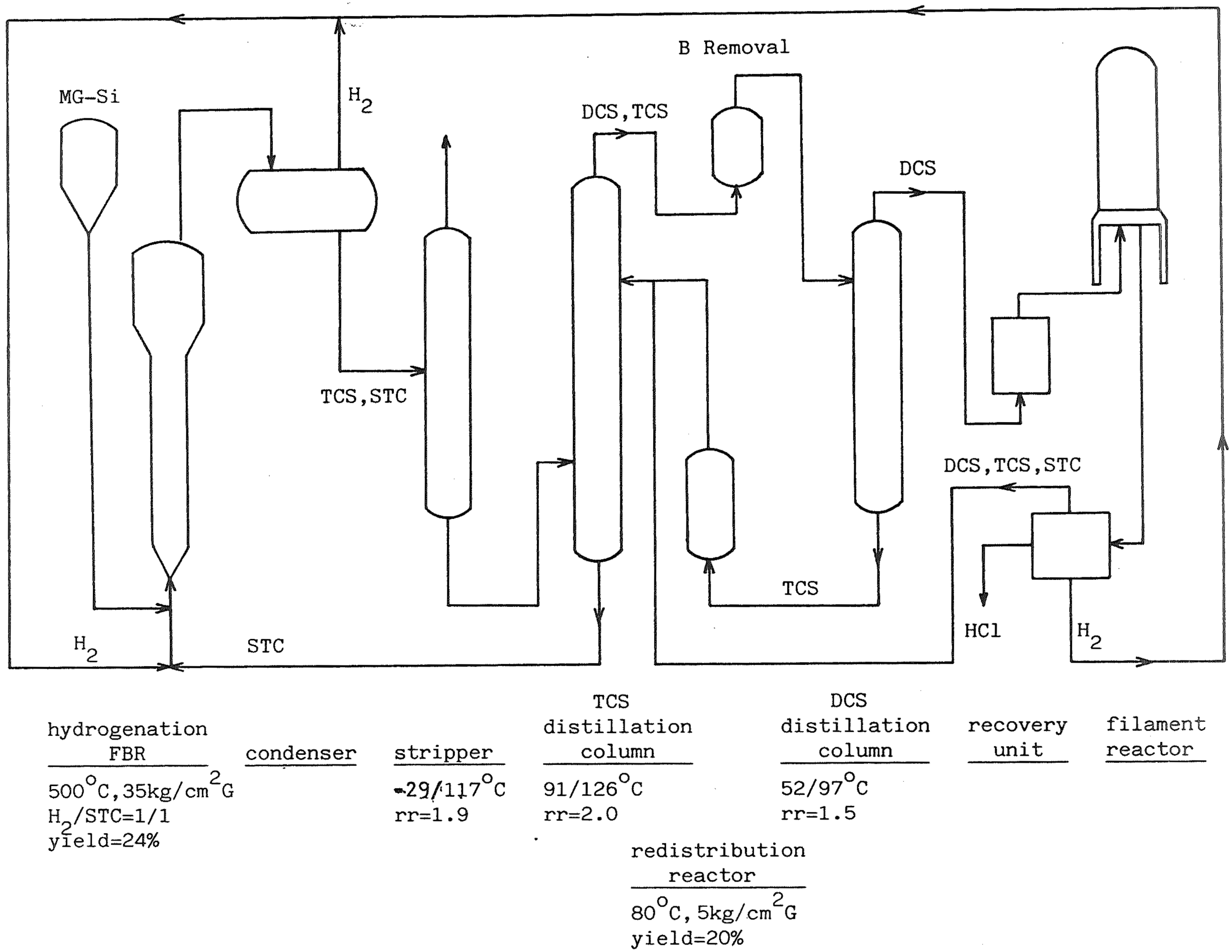


Fig. 7. DCS-Based Hemlock Filament Process

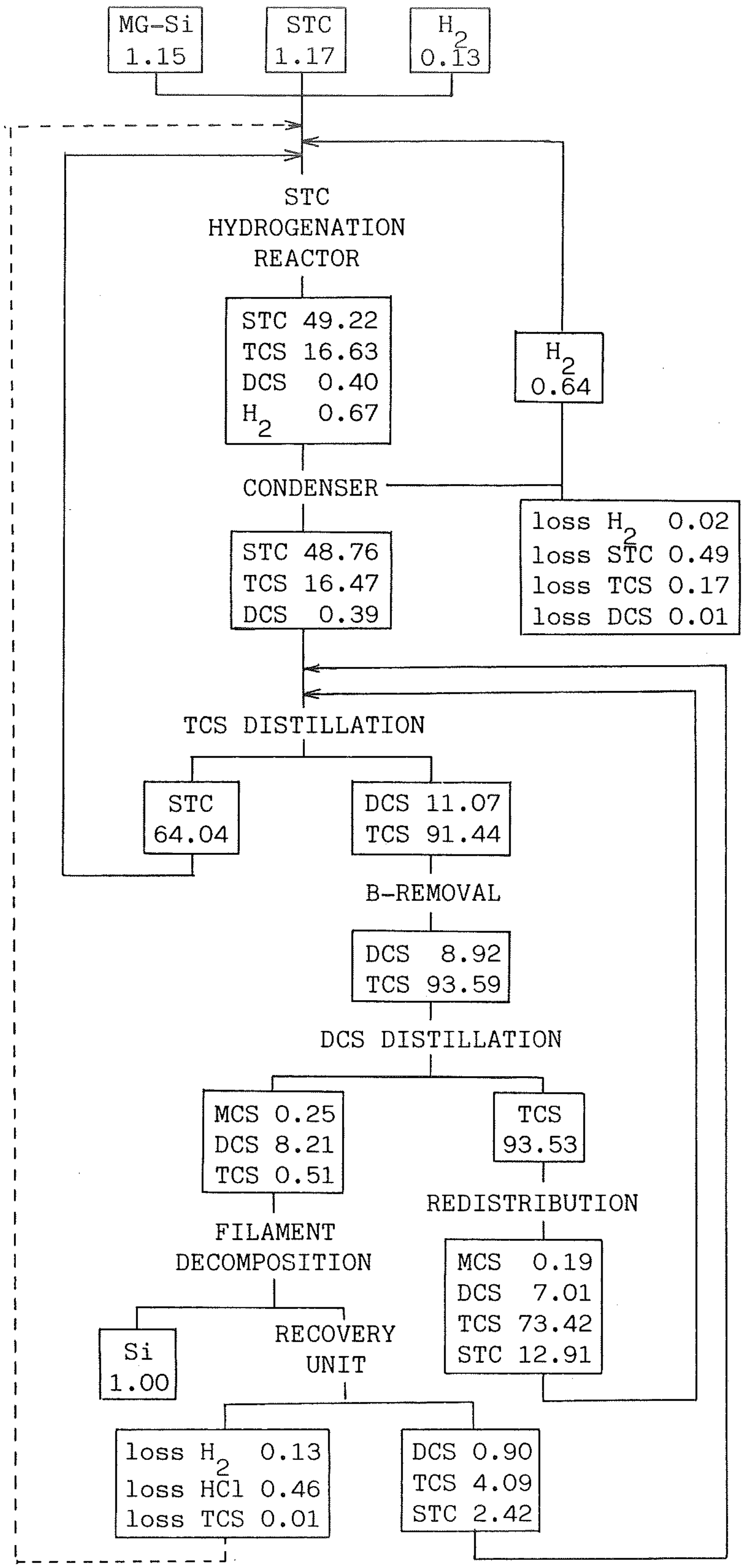


Fig. 8. DCS-Based Filament Process (kg/kg-Si)

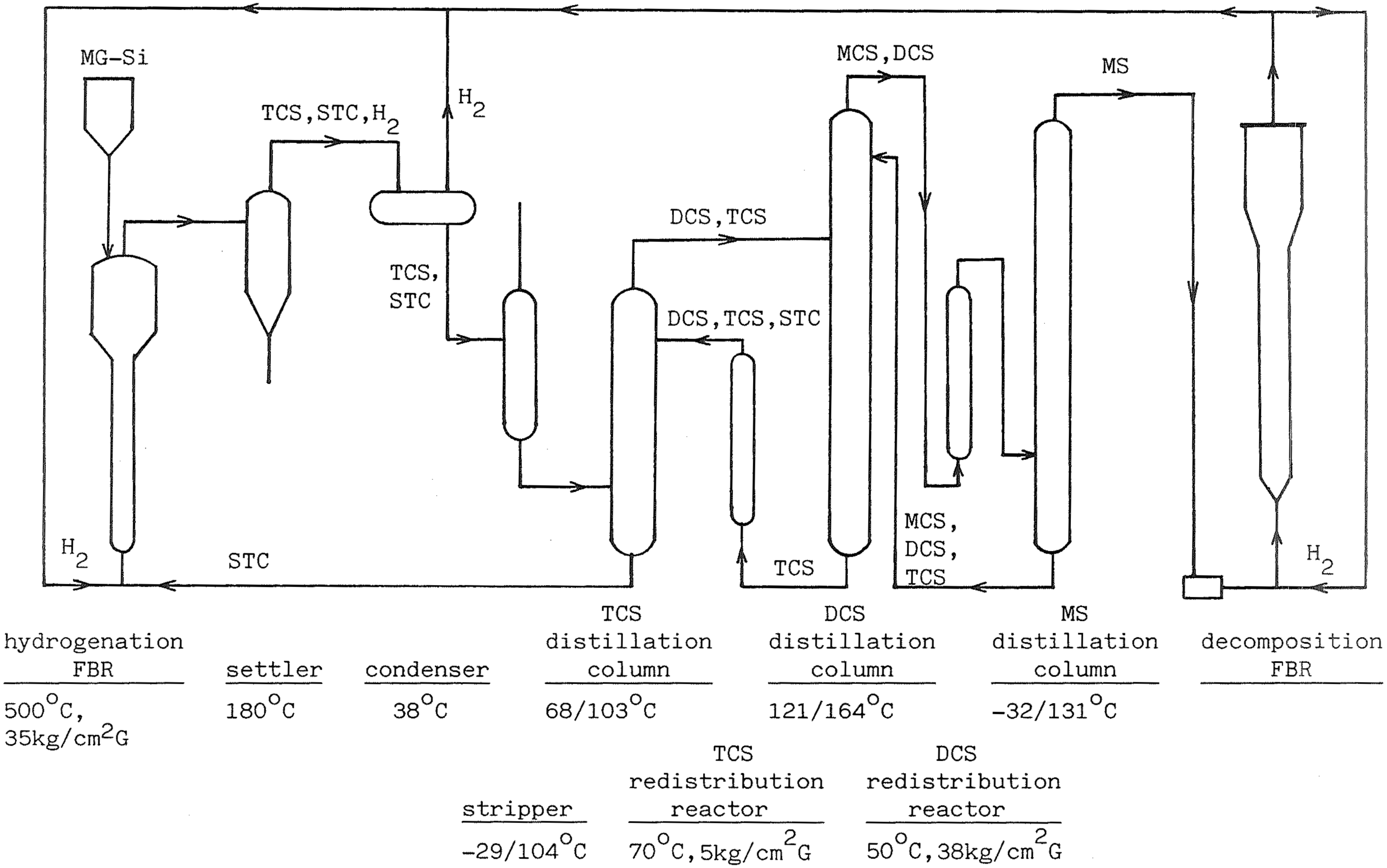


Fig. 9. MS-Based UCC FBR Process

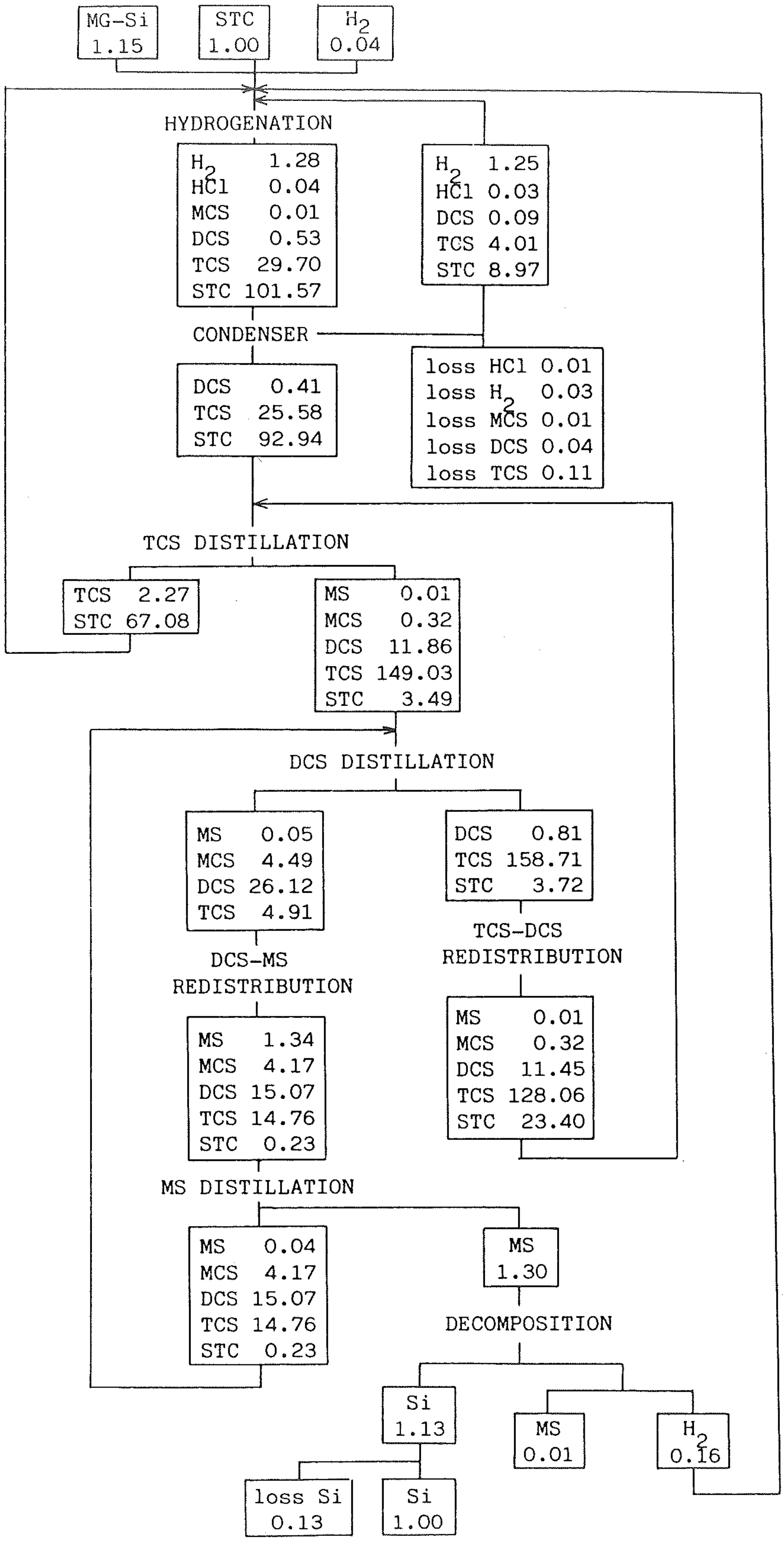


Fig. 10. MS-Based UCC FBR Process (kg/kg-Si)

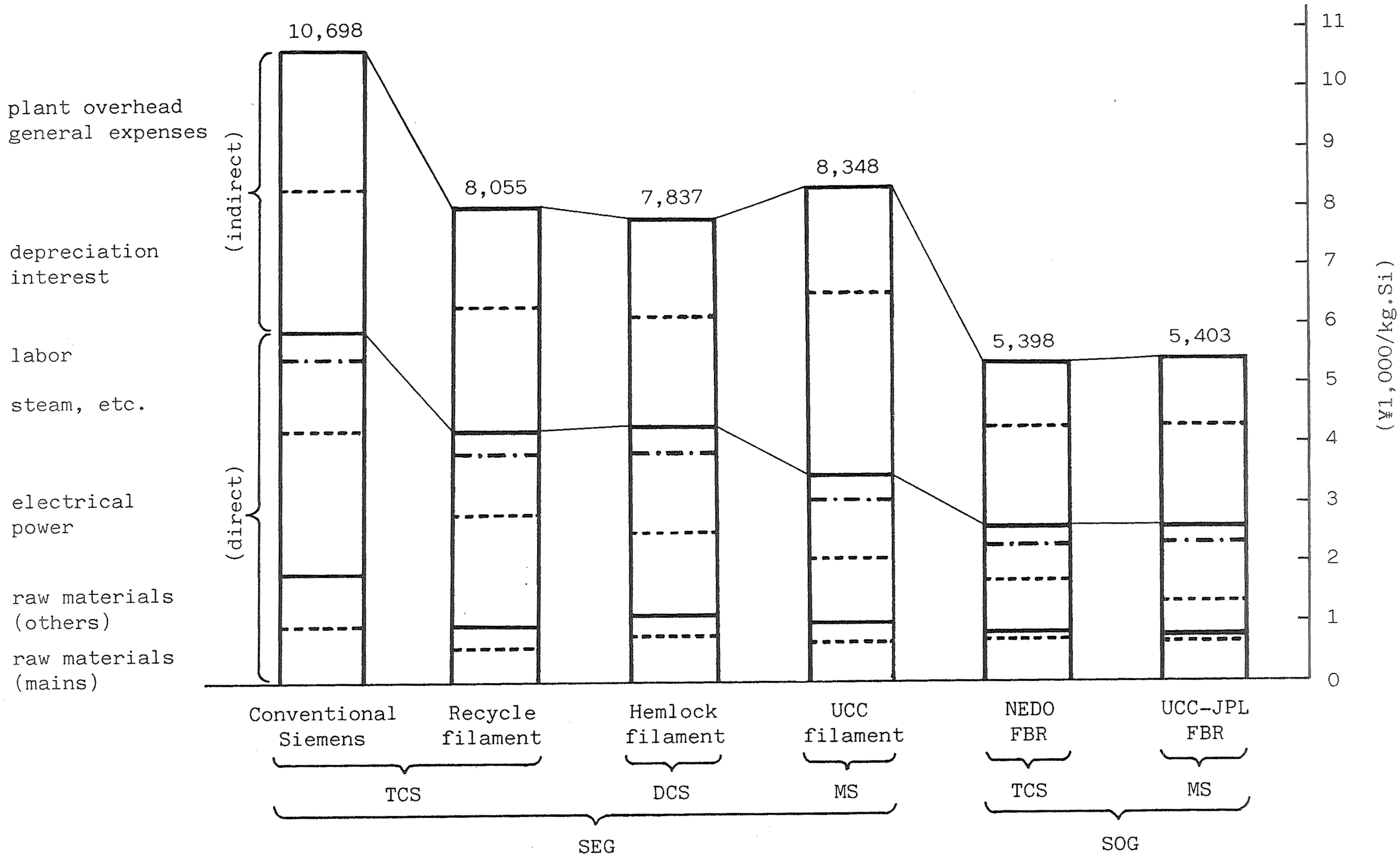


Fig. 11. Production Cost of SEG and SOG-Si (yen/kg-Si) (¥250/$)

Table 1. Process Gases/Liquids in Each Process

(kg/kg-Si)

Material gas		TCS			DCS	MS	
Process		Siemens Filament	NEDO FBR	Recycle, Filament	Hemlock Filament	UCC-JPL FBR	UCC Filament
TCS Synthesis	Process	chlorination	STC→TCS	STC→TCS	STC→TCS	STC→TCS	STC→TCS
	Feed	17.50	105.16	77.50	66.24	131.81	131.81
	Product	15.50	21.03	15.50	16.63	29.70	29.70
TCS redistribution	Feed	---	---	---	93.53	163.24	163.24
DCS redistribution	Feed	---	---	---	---	35.57	35.57
TCS distillation	Crude	17.50	105.16	77.50	159.15	282.17	282.17
	Recovery	37.00	23.75	37.00	7.40	---	---
	Distillate	41.00	25.69	41.00	102.51	164.70	164.70
DCS distillation	Feed	---	---	---	102.51	198.97	198.97
	Distillate	---	---	---	8.97	35.57	35.57
MS distillation	Feed	---	---	---	---	35.57	35.57
	Distillate	---	---	---	---	1.30	1.30
Decomposition	Feed	41.00	25.69	41.00	8.97	1.30	1.30
	H_2/Mat. ratio	5~10	1.5	5~10	15~24	0~4	---
Recovery	Chlorosilanes	38.44	24.17	38.44	7.41	---	---
	Concentration	6~10 %	32 %	6~10 %	1.5~3 %	---	---
Waste	Loss	3.01	0.73	0.41	0.67	0.01	0.01
	Treatment	neutralization	←	←	←	combustion	←
	NaOH	3.00	0.72	0.36	0.63	---	---

Table 2. Manufacturing Cost Estimate for Polycrystalline Silicon (¥/kg)

basis: 1,000t/y

Quality	SEG								SOG				Remarks
Material gas	TCS				DCS		MS		TCS		MS		
Process	Siemens Filament		Recycle-Filament		Hemlock Filament		UCC Filament		NEDO FBR		UCC-JPL FBR		
Raw Materials	requirement		requirement		requirement		requirement		requirement		requirement		
MG-Si (¥300/kg)	3.70kg	1,110	1.06kg	318	1.15kg	345	1.15kg	345	1.13kg	339	1.15kg	345	
STC (¥250(Δ¥120)/kg)	Δ13.00kg	Δ1,560	0.58kg	145	1.17kg	293	1.00kg	250	0.76kg	190	1.00kg	250	
H_2 (¥100/m³)	5.40m³	540	1.19m³	119	1.41m³	141	0.39m³	39	1.13m³	113	0.39m³	39	
Others		1,744		350		350		350		76		70	
Sub total		1,834		932		1,129		984		759		704	
Utilities													
Power (¥15/kwh)	160kwh	2,400	125kwh	1,875	90kwh	1,350	70kwh	1,050	61kwh	915	40kwh	600	
Steam, etc.		1,020		800		1,200		800		404		800	
Others										22			
Sub total		3,420		2,675		2,550		1,850		1,341		1,400	
Other directs		180		180		180		180		180		180	
Labor, 6 M-¥/man.y	75men	450	75men	450	75men	450	75men	450	50men	300	50men	300	
Direct cost total		5,884		4,237		4,309		3,464		2,580		2,584	B
Depreciation, Interest		2,400		2,000		1,760		3,000		1,600		1,600	A×0.2=C
Plant overhead		1,019		767		746		795		514		514	(B+C)×0.123
Indirect cost total		3,419		2,767		2,506		3,795		2,114		2,114	
Total manuf. cost		9,303		7,004		6,815		7,259		4,694		4,698	D
General expenses		1,395		1,051		1,022		1,089		704		705	D×0.15
Product cost		10,698		8,055		7,837		8,348		5,398		5,403	
Plant investment (M-¥)	12,000		10,000		8,800		15,000		8,000		8,000		A

Note: ¥250/$

omit

DISCUSSION

MAYCOCK: When you use the 15 yen/kWh for the electricity cost, is that your estimate of the average or the actual cost in Japan?

SHIMIZU: That is the industrial cost.

MAYCOCK: I wondered, because there is a factor of two in that number in the world now.

SHIMIZU: It is much cheaper in the United States. In general, other cost estimates can still vary from my estimate.

LEIPOLD: You mentioned that the quality of the silicon from the NEDO fluidized-bed reactor process is proven. Can you define the word "proven" further with any analyses?

SHIMIZU: This silicon granular material is now being used in the casting process.

PELLIN: Can you give concentration levels of boron and phosphorus?

SHIMIZU: The resistivity is about 10 ohm-cm.

AULICH: What are the next goals in your project? You said that 10 MT/year is being produced. What are the future plans?

SHIMIZU: I'm not sure I can answer. This question is best asked of Dr. Noda.