An Energy Balance Study of a Newly Developed Recycling System for Waste Plastics

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Contents

Abstract

This paper covers a newly developed recycling system for waste plastics such as waste FRP boats. This issue of abandoned waste FRP boats becomes one of the social problems due to their environmental impact. The authors developed the recycling system in order to carry out the actual recycling of FRP boats, featuring its economical advantage as the first priority with further consideration of social needs.

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In this system, the resin in waste FRP is degraded by supercritical water to be recycled as valuable raw materials, while glass fiber can be recycled by being melted at 1400~1500℃ and molded into some shapes of products. Necessary supercritical water and electrical energy are to be supplied by its generating system using fuel of heat decomposed gas of waste plastics. In this paper, the authors are reporting its energy balance from the following economic point of view by which this system should be evaluated.

(1) Fairly good in economics because of much more surplus electric power generated to be sold.
(2) Good in power cycle efficiency.

The features of this system are as follows;

(3) It is possible to recycle both waste FRP and general waste plastics.
(4) It is virtually unnecessary to use landfills.
(5) The system does not pollute. There is no likelihood of generating dioxin.
(6) Pretreatment such as washing, sorting and so forth would not be necessary for waste materials .

1. Introduction

The historical development of disposal of waste fiber reinforced plastic (FRP) boats is as follows. More than 40 years ago, FRP was successfully applied to the main parts of boat structures and fairly long time passed until the treatment of waste FRP boats became a social problem. From time to time some studies on processing or treatment with waste FRP such as waste FRP boats have been carried out since around 1973 (Showa 48, Showa: Japanese way of describing period). Coming into 1985~1994 (Showa 60s), this project was undertaken seriously and some reports[1)] were published on new equipments which had been developed for treatment and recycling of waste FRP boats and related waste materials. However, these treatments are not currently used in practice because of the high cost.

Originally, the common reclaiming method for waste material has been "landfill". Even today, landfill is still the most common reclaiming method despite of the emphasis on recycling issues. On the other hand, because of the lack of space for landfill and the existence of regulations such as "Recycling Law" effective in

Table 1 Laws Related to Waste Materials (within Japan)

Laws	The date published
Law for Promotion of Utilization of Recyclable Resources (Recycling Law)	Apr. 26, 1991(Heisei 3)
Waste Management and Public Cleansing Law (renewed)	Oct. 5, 1991(Heisei 3)
Law for promotion of management with specific facilities for industrial waste treatment (Arrangement Promotion Law)	May 27, 1992(Heisei 4)
Temporary Law for Rationalization of Utilization of Energy Resources and Promotion of Business Activity Related to Utilization of Recyclable Resources (Law for Assisting Energy- Saving and Recycling)	Mar. 31, 1993(Heisei 5)
Law for Promotion of Sorted Collection and Recycling of Container and Packaging	June 16, 1995(Heisei 7)
Basic guideline for promotion of recycling of materials which meet with the sorting standards	Dec. 15, 1995(Heisei 7)
Products Liability Law (PL Law)	July 1, 1995(Heisei 7)

1993 (Heisei 4, Heisei: Japanese way of describing period) (Table 1), the trend of recycling of waste material is becoming increasingly popular from year to year. The current requirements for the treatment of waste materials can be described in the following key-words from (1) to (5).

(1) Recycling (almost mandatory)

(2) Protect the environment (particularly the control of dioxin generation in case of garbage incineration)

(3) Preserving of our limited natural resources

(4) Reduce the amount used for landfill

(5) Reduce the cost of waste treatment

As seen in Appendix 1, many studies on waste FRP recycling have been tried and they turned out to be technologically feasible. The priority of the key-words mentioned above concerning waste materials treatment are from (1) to (4) at present. These are much crucial issues than (5), but the major determining factor is definitely (5), namely economics. Accordingly, the authors have tried to build up a recycling system which provides favorable economics while giving due consideration to all aspects of all the key words from (1) to (5). In this paper, some main points of the developed recycling system are introduced and some analysis of the results of the energy balance are reported.

2. Process flow of the system

An overview of the newly developed waste plastic recycling system is shown in Fig.1. This system consists of the two units as follows;

2.1 Generating unit fueled by waste plastics

In this unit, waste plastics are thermally decomposed to generate gas which can be used as fuel to produce supercritical water and electricity.

(1) Thermal decomposition of waste plastics

Utilizing the supercritical water produced at the boiler, waste plastics are decomposed at 300～450 ℃ in air evacuated state in the thermal decomposing equipment. Some amount of air can enter into the equipment during waste plastics charging work, but it becomes higher in pressure than outside because of the thermal decomposition inside the equipment. The air can be evacuated outside in the beginning step of the thermal decomposition.

(2) HCl removing from thermally decomposed gas

HCl is separated from the gas in HCl remover by wet-type absorption method.

(3) Supercritical water production

Utilizing thermally decomposed gas as fuel after HCl remover, supercritical water (22.5 MPa, up to 374.1 ℃) is produced in the boiler.

(4) Supercritical water supply to supercritical processing equipment

Some portion of supercritical water is supplied to the supercritical processing equipment.

(5) Electricity generation by surplus portion of supercritical water

After supplying the supercritical water to both supercritical water processing equipment and thermal decomposition equipment, the rest portion of supercritical water is introduced to a steam turbine itself (System 1) or to both a steam turbine and a gas turbine (Combined System, System 2) to generate electricity.

In case of applying this system to a ship, this combined system (System 2) can be chosen to supply the driving energy by the gas turbine.

(6) Electric power supply to melting furnace

Using a portion of generated electric power, inorganic material of waste FRP is processed through high temperature melting and cooling to make molding.

(7) Effective utilization of surplus electric power

Surplus electric power is to be sold. In case of facilities in the ocean, it is impossible to sell it and it can be used to save energy for Hydrogen deposited metal alloy or for some other accumulating system.

2.2 Waste FRP processing and recycling unit

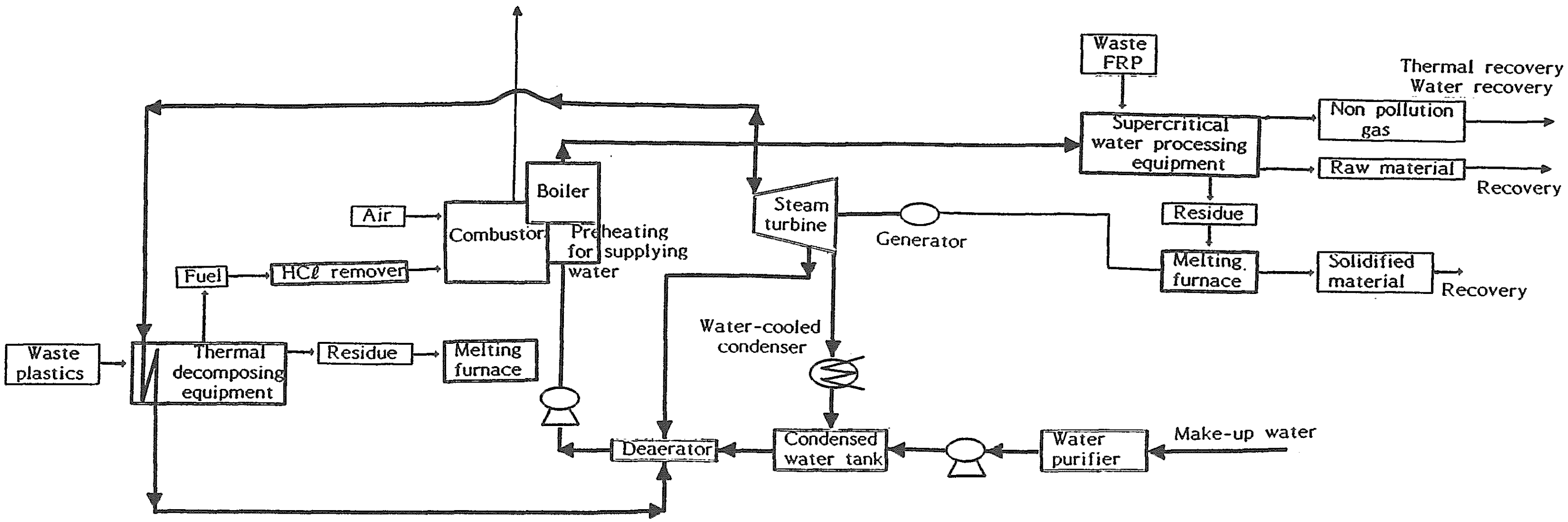
Waste FRP treating systems have been technically established based on the previous studies and various attempts were also made to reach relatively higher level regarding recycling technologies. In case of waste FRP materials, particular characteristics are observed as follows;

(1) Their formulations and ingredients are mostly uncertain.

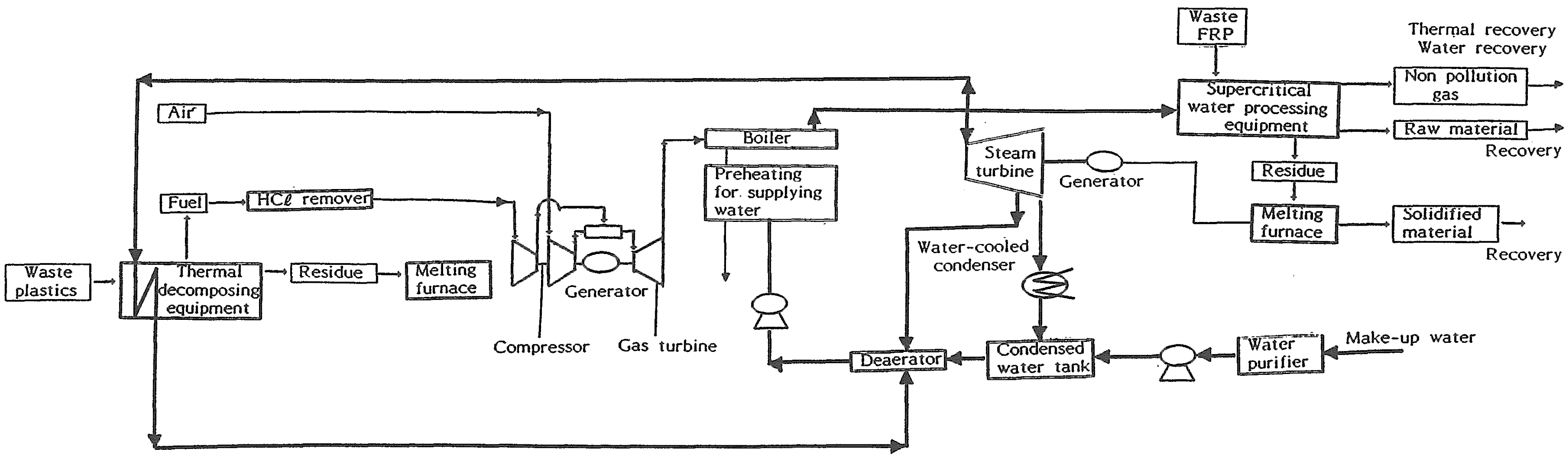
(2) They have been usually spoiled with some contaminants.

(3) It is difficult to separate materials when intermingled with other materials.

In case of this system, the following two technologies adaptable to those characteristics



(a) System 1



(b) System 2

Fig.1 Waste Plastics Recycling System

were applied to make waste FRP recycling. Although this attempt of studying waste FRP recycling technology is at present in the beginning stage, it is expected to become one of the practically available technologies in the near future.

(1) Waste FRP degradation by supercritical water processing

Organic material portion (mostly resin) of waste FRP is degraded by supercritical water processing recovering valuable raw materials.

(2) High temperature melting (1400～1500 ℃) and cooling down process for waste material

Inorganic material portion (mostly glass fiber) of waste FRP is melted at 1400～1500 ℃ to be poured into molds and recycled into new products.

3. Key technologies in this system

3.1 Thermal decomposition technology

Waste materials are usually spoiled with contaminants and many recycling methods require a washing process. As FRP products were made from a plurality of components, the separation process is also necessary. However, in the thermal decomposition method, organic material portion can be degraded and inorganic material portion can be recovered as residue. The washing process consequently in case of some minimal contamination and separation process can be eliminated. Therefore, it has an advantage from the economic point of view. Today, the thermal decomposition technologies with plastics including FRP are already established.[2)3)] Table 2 shows the data of combustion heat quantity for various plastics. Unsaturated Polyester resin used for FRP boats has combustion energy of 7,360 kcal/kg as the same level as those of other plastics, 5,000 ～10,000 kcal/kg. Thermal recycling decomposing waste plastics of up to 17 million tons a year in production would be very effective and useful from this point of view.

Table 2 Calorific Value of Plastics

Plastics	Higher calorific value kcal/kg
Unsaturated Polyester Resin	7,360
Epoxy Resin	7,640
Polyethylene	11,070
Polypropylene	11,040
Polystylene	9,880
Polyvinylchloride	5,420
Polyurethane	6,850
Polyethylene Terephtalate	5,470

3.2 Generating technology applying supercritical water

In a thermal power station of the newest steam turbine, the conditions of the steam pressure and temperature are usually 25 MPa and 566 ℃ respectively in supercritical state. Therefore, production and utilization of supercritical water can be possible without any technical problems introducing this current technology.

No power station with a steam turbine in supercritical state was found in case of combined system, and the different type of heat exchanger from those commonly used should be applied. There is no particular technical problem even in such a case. Generating technologies with steam turbines or gas turbines being already established can be applied for this system.

3.3 Technology for degradation by supercritical water

Supercritical state is defined as a state exceeding limiting pressure and temperature (critical point) in which gas phase and liquid phase can coexist, and the material has both characteristics of gas (diffusion etc.) and liquid (solubility etc.). That is to say, it has low viscosity and high diffusion coefficient. Moreover, it can be used as a catalyst in chemical reaction because, in such a state, reaction velocity is remarkably promoted and ion products and electric inductance can be changed by controlling pressure. Based on these characteristics, extraction, separation, cleaning and condensation with some ingredients, supercritical technologies are successfully applied in industries. For instance, Carbondioxide (CO_2) in supercritical state has the critical point of 7.38 MPa and 31.1 ℃ which is actually low and is already applied in industries.[4)] This technology is widely applied to cosmetics and perfume industries (extraction of raw materials and natural perfumes) and also to materials, machinery chemical, energy, medicine and food industries.

On the other hand, the application of

supercritical water technology is still at the stage of research because of its higher critical point of 22.5 MPa and 371.4 ℃. Some studies, however, have been made on extracting some raw materials from FRP and other plastics.[5] At present, though there are many unknown facts with respect to these technologies, taking into account the rate of progress, it can be expected that they will be utilized in industries in a couple of years. Raw materials of high quality can be recovered through these technologies to be established.

3.4 Melting Technology for waste materials

Melting treatment has relatively a long history in municipal's waste water soil treatment in processing ash from incineration and in temporary process with garbage. Particularly, according to the improvement of the Recycling Law, the middle stage processing technology for fly ash from incineration became one of mandated technologies of the Ministry of Health and Welfare. This requirement encouraged the development of much new applications such as stabilization of solids[6], modification[6], dioxin, heavy metal processing and studies of cooling down processes.

This method of melting technology is effective to reduce the waste materials in volume solidifying them into about 10% even for landfill. However, if it is possible to make melted solid of residue recyclable, it will be a very effective method of reducing space requirement for landfill area and also be beneficial and promising for saving resources by recycling. Today, actual applications with melted solids are blocks, road base and ground levelling material.[7]

Melting technology with waste FRP has just started by experimenting in melting at 1500 ℃. As organic material portion of resin is burned out until about 500 ℃, only inorganic portion of glass fiber is melted. It is reported that there is no problem in the melting process itself because the experiment of melting glass fiber up to 1000 ℃ proved to be successful.[8] There are also some advantages in case of waste FRP such as good consistency in its components, no heavy metal leakage and no Chlorine element causing dioxin problem. Therefore, there is almost no problem in quality consistency and safety with the recycled products, which will become acceptable as promising products if they are harmonized with existing material makers and taken into appropriate logistic routes.

Melting temperature of 1400～1500 ℃ level can be obtained by fuel burning or electric power. In case of electric power which the authors have chosen for this system, several methods are recently available such as plasma method, arc method, electric resistance method and so forth.

4. Energy balance

4.1 Establishment of various efficiencies

Necessary indexes and figures such as various efficiencies for calculating energy balance were determined as follows. In determination, careful consideration was given for taking smaller figures during energy calculations.

(1) Fuel yield from thermally decomposed gas: 0.8

A 20% loss is considered to be more reliable because of lack of experience in the past, although it may be possible to use the combustion heat of thermally decomposed gas as 100%.

(2) Air excess rate during boiler combustion: 2.1

This rate was taken as rather large than usual. The larger it becomes, the lower the boiler temperature goes down taking the proper condition for heat efficiency.

(3) Inner efficiency in steam turbine η : 0.8

This efficiency becomes bigger as the size of a steam turbine increases. The size of steam turbine in this system was a relatively small class of 10,000 kw. Therefore, the authors adopted the lowest inner efficiency taking from that of currently used steam turbines.

(4) Supercritical water amount to be supplied to its processing equipments: 10 times amount of steam quantity necessary for raising FRP temperature up to 390 ℃

390 ℃ was chosen for FRP processing temperature based on the experimental data[2]. It was not certain concerning necessary amount of supercritical water to raise FRP temperature up to 390 ℃. 10 times amount of calculated supercritical water was considered to be necessary for raising FRP temperature up to 390 ℃.

(5) Water supply to deionized water producing equipment: Equal amount to that of supplying supercritical water (only in use of supercritical water)

Equal amount of water to that of supercritical water should be supplied. Some loss will be expected in practice, but it is not so large as to influence the result of calculation.

(6) Electric power consumption at plasma melting equipment: 0.7 kw/(kg/hour)

Electric melting equipments adopted in this system will be plasma method, arc method, electric resistance method and so forth as mentioned earlier. The recycled products are different depending on the equipment being used. At this time, the recycled products are not decided yet. The authors, therefore, do not recommend the specific equipment. In this paper, plasma equipment is adopted for convenience and the electric power consumption was determined based on its published data.[9]

(7) Exhausted gas temperature from the boiler: 170 ℃

The gas should be exhausted in the temperature range not to generate white smoke absolutely.

4.2 Examples of energy balance calculation

Taking the assumption on the treating amount of waste FRP and kinds of waste plastics, energy balance was calculated for System 1.

4.2.1 Establishment of treating conditions

(1) Treating amount of waste FRP

In this system, the authors assume the figure of 4,000 tons (as for FRP) equal to about 10% amount of shipbuilding a year as one year treatment for calculation. (FRP production in Table 3) If the treating work is 12 hours a day and 240 working days a year, waste FRP treating amount will become 1.4 tons per hour.

(2) Treating amount of waste plastics

The waste plastics thermal decomposition treating amount is assumed to be 10 tons for one hour. Making 24 hours service with 240 working days a year, the treating amount a year will become 57,600 tons.

Though almost every kind of plastics will be acceptable as fuel in this system, PET resin (Polyethylene Terephtalate) was chosen because of its relatively lower calorific value (Table 2) in the thermal calculation. Thermal decomposition temperature is dependent on its components and 450 ℃ was assumed where every kind of plastics can be thermally decomposed.

4.2.2 Energy balance calculation

Fig.2 shows the results of energy balance calculation for System 1, and its calculation bases and processes are as follows.

(1) Thermal decomposition of waste plastics

PET (10,000 kg/hour) is thermally decomposed at 450 ℃ sealing off the equipment from outside air utilizing supercritical water produced in the boiler. Air can be included in it during charging waste plastics into the equipment, but the air will be evacuated from the equipment by internal higher pressure generated from the thermal decomposition. 5,500 kcal/kg and 2 kj/(kg・℃) were used in the calculation as the calorific value of PET's thermally decomposed gas and as its specific heat content respectively. As the transferring rate to fuel was 0.8, the calorific value available during combustion would become 4,400 kcal/kg.

(2) Supercritical water production in the boiler

Table 3 End Uses for FRP Products

(unit : ton)

Application / year	Const-ruction	Resi-dential	Marine	Trans-portation	Tank Vessels	Industrial Equipment	Consumer Products	Others	Total
1992	34,800	185,500	30,500	24.500	51,200	58,100	36,300	12,800	433,700
1993	33,300	204,400	28,800	22,500	40,400	54,700	36,000	11,900	432,000
1994	38,300	211,500	28,800	21,600	54,900	54,900	35,900	11,600	442,600
1995	41,500	218,600	24,200	21,700	57,600	57,600	39,100	12,400	458,200
1996	45,100	230,100	24,100	22,300	60,100	60,100	42,400	13,000	479,500
(%)※	(9.4)	(48.0)	(5.0)	(4.7)	(8.9)	(12.5)	(8.9)	(2.7)	(100.0)

※ ratio to total in 1996

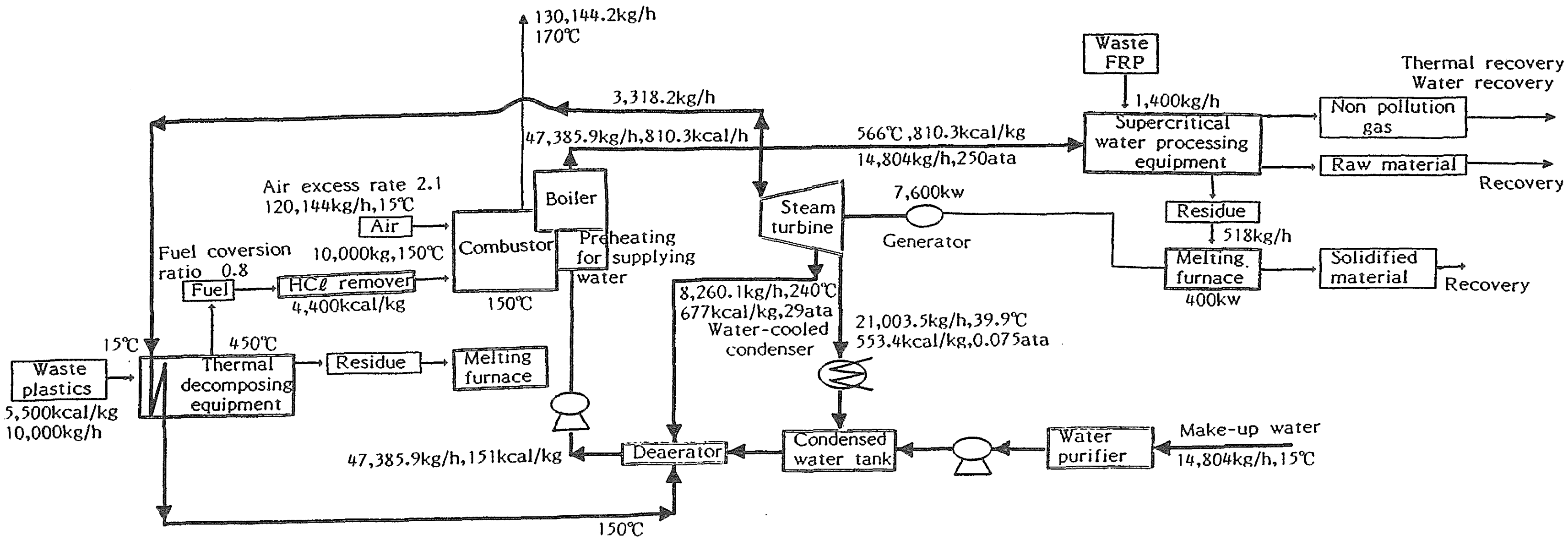


Fig.2 Heat Mass Balance Calculation (System 1)

Thermally decomposed gas, 10,000 kg/hour, generated at 450 ℃ was introduced into combustion furnace becoming at 150 ℃ after being processed through HCl remover. In the boiler, it is fully burned with enough air (excess rate 2.1) to heat up deionized water (47,385 kg/hour) producing supercritical water (47,385.9 kg/hour) of 25 MPa at 566 ℃. Its heat content was 810.3 kcal/kg. This supercritical water was distributed into three pieces such as the thermal decomposing equipment, the supercritical water processing equipment and the steam turbine. Exhausting gas (130,144.2 kg/hour) was discharged at 170 ℃ avoiding white smoking problem from it.

(3) Supercritical water supply to the thermal decomposing equipment

Supercritical water amount for supplying to the thermal decomposing equipment was decided to be 3,318.2 kg/hour necessary for keeping PET temperature at 450 ℃.

(4) Supercritical water supply to the supercritical water processing equipment

The FRP material used here in the calculation had 70% of resin content and its thermally decomposed gas was assumed to contain 48% of Carbon and 4% of Hydrogen in it with 4,930 kcal/kg of calorific value remaining 37% of residue after thermal decomposition.[10] Supercritical water amount for supplying to the supercritical water processing equipment was determined to be 14,804 kg/hour, 10 times as much as the necessary amount in order to keep FRP (1,400 kg/hour) temperature at higher than 390 ℃.

(5) Supercritical water supply to the steam turbine

After sending the rest portion of supercritical water (29,263.7 kg/hour) to the thermal decomposing equipment and the supercritical water processing equipment, the steam turbine is operated. When its inner efficiency is 0.8, electric power generated became 7,600 kw. 8,260.2 kg/hour of steam (2.9 MPa, 240 ℃, 677.0 kcal/kg) was sent to the boiler through the deaerator and water of 21,003.5 kg/hour (0.0075 MPa, 39.9 ℃, 553.4 kcal/kg) was returned to the water recovery tank. When not treating with FRP, the supercritical water amount to the steam turbine became 44,067.7 kg/hour to generate the electric power of 12,400 kw.

(6) Necessary amount of electric power for the melting equipment

After treating 1,400 kg/hour of FRP, the amount of residue remaining was 518 kg/hour, corresponding to 37% of FRP to be treated. To make plasma melting process (consuming electric power of 0.7 kw/(kg/hour)) at 1,500 ℃ with this residue, necessary electric power amount was approximately 400 kw.

(7) Water supply to the deionized water equipment

When supercritical water process was operated, 14,804 kg of additional water (15 ℃) was necessary to supply for this system.

4.2.3 Calculation of surplus electric power amount

Table 4 shows the result of calculation of surplus electric power amount when this system was operated under the condition shown in Table 5. As FRP treating was not operated in daytime, supercritical water amount for FRP treatment could be used for the electric power generation. Additionally, as the high temperature melting was also not operated, this portion would be expected to convert to the surplus electric power.

Table 4 Surplus Electric Power

Item \ System		System 1	System 2
Night time	Steam turbine output	7,600 kw	900 kw
	Gas turbine output	0 kw	7,500 kw
	Melting furnace	400 kw	400 kw
	Surplus electric power	7,200 kwh	8,000 kwh
Day time	Steam turbine output	12,400 kw	7,200 kw
	Gas turbine output	0 kw	7,500 kw
	Melting furnace	0 kw	0 kw
	Surplus electric power	12,400 kwh	14,700 kwh
Annual Surplus electric power		56,448,000 kwh	65,376,000 kwh

Table 5 Treating Condition

Treating processes	FRP treating	Waste plastics generation
Waste materials supplied	FRP	PET resin
Annual working days	240 days	240 days
Working hours a day	12 hours (night time)	24 hours
Treating capacity	1.4 ton/hour	10 ton/hour
Annual treating amount	4,000 tons	57,600 tons※

※ Equivalent to 720 million PET bottles

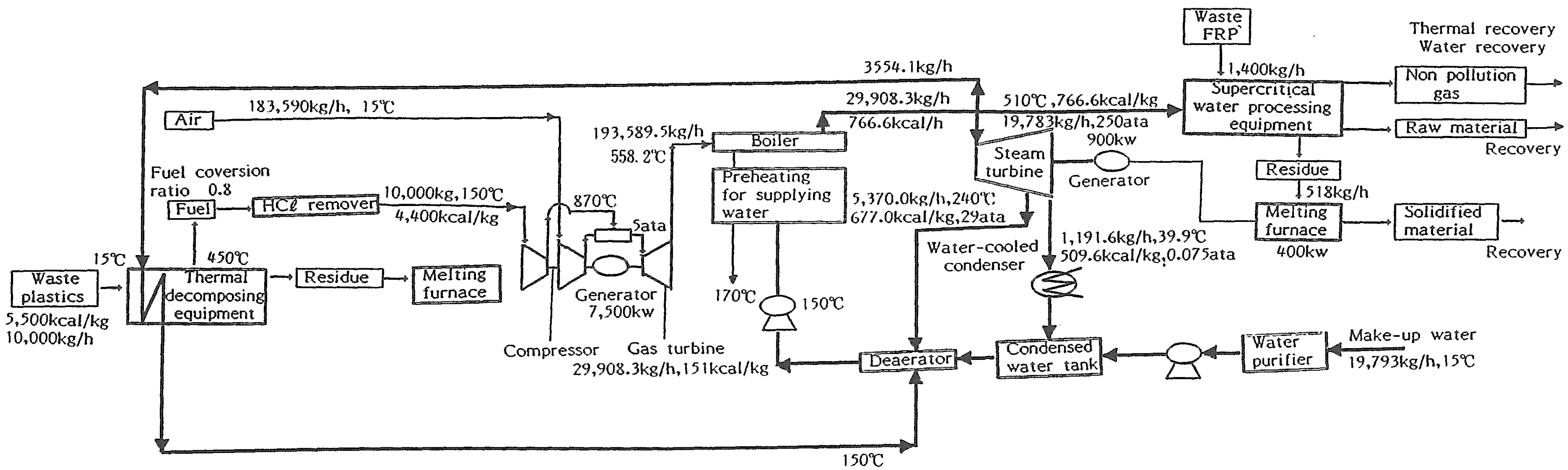


Fig.3 Heat Mass Balance Calculation (System 2)

The calculation result considering those conditions showed that an annual surplus electric power amount became 56,448,000 kw.

Fig.3 shows the calculation result of energy balance for System 2, and an annual surplus electric power amount is shown in Table 4.

4.2.4 Power cycle efficiency

Power cycle efficiency is defined as follows:

$$\text{efficiency} = \frac{\text{Energy used in the steam turbine to generate electricity Power cycle}}{\text{Energy※ given to this system}}$$

※ In this case, this means energy of thermally decomposed gas from PET

These are 19.6% and 23.0% for System 1 and System 2 respectively.

5. Running cost estimate

Running cost was estimated for System 1 when operated under the treating conditions described in the previous section 4. The cost of actual utilities' (fuel, electricity, and city-water) and labour were taken into account, because the depreciation cost and income from sales of recycled products were uncertain, these factors were not included in the running costs. In this report, ¥125/US$ is taken as the rate of exchange.

(1) Fuel cost

Fuel is waste plastics in this system. The waste materials at present cannot be accepted by processor without paying some handling fee and these costs vary, but are thought to be at least ¥10/kg (US$0.8/kg). Assuming it as ¥10/kg (US$0.8/kg), ¥576 million (US$4,608,000) will be generated as income if 57,600 tons of waste plastics is treated.

(2) Electric power expense

As described above in calculating the surplus electric power, annual surplus electric power amount is 56,448,000 kw. Electric power companies can purchase electricity and in case of garbage generation, taking ¥5/kw•hour (US$0.04) as the purchase price based on the data as shown in Table 6, the income becomes ¥282,240,000 (US $2,257,920).

(3) City water expense

It is necessary to supply the amount of water equivalent to that of supercritical water used. Under the condition taken in this system, necessary amount is 19,793 kg/hour. The annual amount becomes about 57,000 tons (57,000 m^3). Appling the city water price (for example, in Mitaka-city, 1997) in the calculation, the annual expense became ¥37,100,000 (US$296,800) (including expense for waste water treatment).

(4) Labour cost

10 people will be relatively enough for each process among four processes (thermal decomposing, generating, supercritical water processing and high temperature melting). Annual labour cost for one person is estimated to be ¥6,000,000 (US$48,000) and the number of workers including 10 other members is 50. Annual labour cost then becomes ¥300,000,000 (US $2,400,000).

As discussed above, the annual expense is as follows:

Table 6 Garbage Generation Unit Price

(1996 (Heisei 8)) ¥/kwh(US$/kwh)

Company \ hours	Summer Season 8:00~20:00	Other Season 8:00~20:00	All Season's Other Times
Hokkaido Electric Power Co.	10.60(0.085)	9.60(0.077)	4.40(0.035)
Tohoku Electric Power Co.	11.20(0.090)	10.00(0.080)	5.70(0.046)
Tokyo Electric Power Co.	12.80(0.102)	12.20(0.098)	4.60(0.037)
Chubu Electric Power Co.	13.61(0.109)	13.20(0.106)	2.61(0.021)
Hokuriku Electric Power Co.	6.70(0.054)	6.20(0.050)	5.00(0.040)
Kansai Electric Power Co.	12.96~13.86 (0.104~0.111)	9.68~10.34 (0.077~0.083)	5.45~5.83 (0.044~0.047)
Chugoku Electric Power Co.	9.20(0.074)	8.70(0.070)	7.40(0.059)
Kyuushuu Electric Power Co.	12.80(0.102)	11.40(0.091)	5.50(0.044)
Okinawa Electric Power Co.	13.10(0.105)	12.40(0.099)	3.20(0.026)

Fuel cost	Income	
	+ ¥576,000,000	(US$4,608,000)
Electric power expense	Income	
	+ ¥282,240,000	(US$2,257,920)
City water expense	Expenditure	
	− ¥ 37,100,000	(US$ 96,800)
Labour cost	Expenditure	
	− ¥300,000,000	(US$2,400,000)
balance	+ ¥521,140,000	(US$4,169,120)

6. Features of this system

(1) Recyclable system with waste FRP and waste plastics.

It is characteristic that it can meet current worldwide needs with respect to resource and energy savings in this system, because it converts waste FRP to raw materials and melted solid products while the thermal recycling of waste plastics generates fuel.

(2) Excellent economics

It is possible to have a viable business with this system because some considerable income can be expected from electric power sales and handling fee for waste plastics acceptance.

(3) Acceptable power cycle efficiency

As the usual power cycle efficiency of garbage incinerating generation is expected to be 10% at least, it is rather acceptable in power cycle efficiencies of 19.6% and 23.0% in System 1 and in System 2 respectively.

(4) No landfilling

The generation of residue by this system is expected to be so little that there is nothing or only very small amount concerning landfill.

(5) Non-pollution system

It is reported that dioxin generates at the temperature lower than 800 ℃ (under atmosphere) when Chlorine containing materials are burned. When the temperature is elevated up to 850 ℃, it decomposes. The waste plastics handled in this system include all kinds of plastics such as Polyvinylchloride of dioxin generating material. However, no pollution can be made in this system as follows;

① The decomposing temperature is indeed around 450 ℃. As it is done under no oxygen atmosphere, dioxin can not be generated.

② HCl can be separated by HCl remover.

③ Chlorine containing materials other than HCl are burned in gas phase in the boiler. In this case, the temperature becomes definitely above 850 ℃ because of vapour phase combustion. Therefore, there is no reason to be concerned about dioxin generation.

④ Waste FRP usually contains no Chlorine materials, and polluting materials other than dioxin can not be generated because of serious treatments under high temperature and high pressure with supercritical water.

(6) No pre-treatment with waste materials

In these processes of thermal decomposition or decomposition by supercritical water, it is not necessary to wash out some contaminants from waste FRP or to sort out other foreign materials. Therefore, these processes can be eliminated.

7. Conclusion

The authors took the economical advantage as the first priority as described earlier, and tried to build waste plastics recycling system which can meet current needs of society. The initially targeted system has been built as follows;

(1) Fairly good economics
(2) Acceptable power cycle efficiency
(3) No pollution system (no dioxin)

The technical requirements to utilize this system in practice as the final goal are as follows;

(1) Utilization of decomposition technology by supercritical water

Before this utilization is achieved, treatment and recycling will be operated only by high temperature melting process.

(2) Establishment of recycled products by high temperature melting process

(3) It is necessary to refine some connecting technologies among each of the basic technologies.

The authors are also considering that it will be necessary for this system to be evaluated by the another method such as LCA (Life Cycle Assessment). Besides, oils leaked from damaged tankers recently became one of the big social problems and it will be the future subject for this system to be studied on if these oil leak (sea water content ~70%, reduced calorific value and viscous) could be recycled as fuel by this system.

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Appendix 1. Current status of waste FRP recycling technology

FRP is a composite consisting of two

components, fibers of inorganic materials and resin of organic materials (Calciumcarbonate of inorganic material is sometimes used as filler in them). Accordingly, the recycling method can be divided into two ways such as recycling as FRP composite itself and recycling by separating glass fiber and resin (organic component and inorganic component).

1 . Recycling as FRP composite itself (Material recycling)

1.1 Recycling FRP composite molding by partially changing their structures

1.1.1 Recycling to use as fishbeds

It is very welcomed that utilizing waste FRP boats as fishbeds is a very suitable application. They are submerged under the sea after making some change in their structure. It is probably the best application for reusing recycled material, preferably with almost no dismantling. However, there are many technical problems to be solved such as how to fix them to their appointed spot, how to anchor them, how to inhibit corrosion of ballast loaded in the bottom of the boats, and how to avoid sea water from pollution by oil materials adhered to the waste boats to be sunk. There is also a biological problem whether or not fish settle in these kinds of fishbed. There are some examples actually carried out and some sample experiments on these issues. In a certain sample experiment[11], several subjects were raised such as rationalization in oil treating, necessity of scientific investigation on effectiveness of their use as fishbeds, and quantitative strength evaluation of hull structure. However, even if good results are obtained in studying this application, it will be up to the fisheries to specify waste boats which would be used as fishbeds. Furthermore, only large sized waste boats will be discussed for fishbeds. Considering the fact that currently used plastic fishbeds are quite reasonable in price and well suited for this application, there may be no opportunity for waste boats which are mostly small size to find their way in main stream of recycling in this field.

1.1.2 Recycling to building material

As for an idea to use as pipe shaped building material, waste plastics are pressed into flat sheet to be rolled up for easy application. Technically speaking, it can be possible but it will not be realized economically due to the costs for pretreatment and pressing process.

1.2 Recycling by grinding waste FRP into powder

Waste FRP is ground into powder and recycled as the second raw materials for SMC (Sheet Molding Compound), BMC (Bulk Molding Compound) and also as filler or reinforcement. Shredders, granulators, hammer mill and others can be used to granulate and mill. These sophisticated technologies are already exist. The quality specification items requested for use of waste FRP powder are specific gravity, glass fiber length, glass fiber content, metal content, residual Styrene monomer content and so on. It is possible to recycle only good quality waste FRP which is guaranteed in its formulation with no contamination. Such waste FRP is originated within the facilities where FRP products were manufactured, but the amount of waste FRP met with those conditions would be no more than 20% of the whole amount. Besides, the biggest problem in this recycling method is that the recycling has to be repeated when the recycled FRP becomes waste FRP.

Nevertheless, it is possible for this method to be accepted as one of the actual recycling methods under the current status when the Recycling Law becomes effective and recycling is universally regarded as a priority issue.

1.2.1 Recycling to SMC products

SMC is sheet shaped material to be molded. The processes to make SMC are as follows. First, chopped glass roving about 25 mm in length strand is impregnated with the resin compound which was formulated viscosity thickener, filler, inner mold release agent, pigment, etc. to unsaturated Polyester resin and then it is covered on both sides, laminating with Polyethylene sheet. The viscosity of the compound becomes thicker to be stick-free sheet shaped molding compound. The development of recycling technology for application to SMC had the problem of the recycling issue of SMC for automotive. In case of using partly the waste FRP powder as substitute of filler, Calciumcarbonate, the report[12] says that there would be no unfavorable influence on molding's mechanical properties concerning the waste SMC as far as it is used under a certain amount (20%) of the powder in a certain particle diameter range that are made from waste SMC moldings in a certain manufacturing plant. However, it seems difficult to recover the cost of the recycling process.

1.2.2 Recycling to BMC products

In general, BMC is a mixed compound of glass fiber, unsaturated Polyester resins, low profile material, viscosity thickener and filler which can be molded by injection or compression processes. The application are sound fences, piles, U type channels, blocks, manholes and sheet rock.

In case of using partly the waste FRP powder as substitute of filler, Calciumcarbonate, the report[12] also says that there would be no unfavorable influence on molding's mechanical properties from the waste BMC or SMC powder as far as these are used under a certain amount (30%) of the powder in a certain particle diameter range that are made from waste BMC or BMC moldings in a certain manufacturing plant. However, there is the same cost problem as in case of recycling to SMC.

1.2.3 Recycling using waste FRP powder as filler or reinforcement

There is no unfavorable influence on applied products for civil engineering and architectural works when waste FRP chip and powder are applied under limited filling ratio in their formulations. Moreover, it is almost impossible to recover the cost of recycling. Some sample experiments tried are described as follows. There is no negative effect on the properties of pulp-cement boards when 5% of waste FRP powder of a particular particle size in diameter is applied.[12]

As filling rates are increased in case of recycling to resin concrete using partly as substitute of Calciumcarbon hydrate or aggregates (fine sand, medium sand), their flexural strength increases.[13]

When waste FRP powder is applied to cement mortar as substitute for aggregates (silica sand) and the addition of powder is limited in its particle diameter size and in the amount (less than 5%), neither unfavorable influence nor positive improvements were found.[14]

When waste FRP powder applied gypsum as reinforcement limiting the powder to be added in its particle diameter size and in its amount (10%), there is no significant effect on the product's mechanical properties and no positive improvement were found.[13]

2. Recycling separating glass fiber portion and resin portion

2.1 Recycling Treating resin thermally

2.1.1 Utilization of incineration heat

The incineration heat is applicable for some municipalities to use actually garbage incineration heat for warming up the meeting room and also the bath water, but their efficiency rates are not enough. However, the electric power generation with garbage incineration[14] is now becoming popular. It is possible for this technology to become the most promising recycling technology in the future.

In general, the content rate of organic material portion such as resin is 30～60% in FRP, utilization by thermal decomposition is unprofitable from the point of view of energy. Moreover, if the land space for landfilling becomes more available because of the Waste Management and Public Cleansing Law, the incineration can be used more as the method of decreasing volume and the utilization technology of incineration heat must be significantly improved.

2.1.2 Recycling using thermally decomposed gas as fuel

The composition of thermally decomposed products are varied depending on their decomposing temperatures. Oils are mostly recovered in the range of relatively low temperature of 400～500 ℃ usually, gases are mainly recovered in the range 600～700 ℃. Generated gases contain large amount of CO and CHs which are so poor in compressibility as to be inefficient in their storage and transportation. Therefore, the oilification is more desirable for their storage and transportation. The recovering yields and physical properties of oil and gases by thermal decomposition are varied depending on kinds of resins and thermally decomposing temperatures. It is reported[2] that, in case of FRP for boats, the recovery yield is high (57+% to the original resin) and the calorific value is also high enough to make good combustion (gas: higher calorific value 8,938 kcal/Nm^3, oil: total calorific value 9,240 kcal/kg). The recovered oils have many aromatic compounds to be mixed to improve the octane value of other oil.[2] On the other hand, several problems on physical properties of thermally decomposed oils and gases recovered have been pointed out. That is to say, the recovered gases contain more than 40% CO_2 and have poor heat efficiency. The recovered oils also have the disadvantage of strong acidity, low igniting temperature, unfavorable ignition and so on.[2]

The methods to refine recovered oil such as distillation method[10] and metal catalyst method[15] are already covered in previously published reports. The report says that the thermal decomposition in moisture was effective to refine recovered gases.[13] Also recycling technologies recovering raw materials such as phthalic acids[13] and synthesizing methanol[16] have been studied. However, at present, these refining technologies are not high enough to recover the cost involved in their use. There is a report[17] on the possibility of refining thermally decomposed gases by microwave irradiation using the certain effect except thermal effect, although an understanding of the underlying principles requires the further study. If microwave irradiation does not include any thermal effect, this technology can be expected to be helpful in changing the process from toxic materials to non-toxic materials and refining the process as well.

Moreover, one of the new interesting technologies is the treatment by the supercritical fluid. This supercritical fluid is defined as the state beyond the point of particular temperature and pressure where two phases of gas and liquid can coexist. The fluid shows some different properties in diffusion and solution to be applied for ingredients extraction, separation, cleaning, condensing and so on. The fluid of Carbondioxide is already used actually in extraction processes of cosmetic raw materials, natural perfumes and fats. In case of FRP, resin in FRP can be processed into monomers utilizing its rapid hydrolysis performance.[14] However, the critical point of water (22.5 MPa with 374.1 ℃) gives difficulty in equipment and this technology is expected to be used in the year 2000 or later.

2.2 Recycling of glass fibers

Glass fibers are recovered as residues after incineration or thermal decomposition with waste FRP. When resin can not be completely decomposed, some small amount of char remains.

2.2.1 Recycling by powdered glass fiber

(1) Raw material

The residues are powdered to recycle in reuse as recycled glass fibers and other glass products, however, raw material sometimes can not be recycled because of unfavorable contamination from paint coated on FRP and coupling agents with glass fibers. It can not be permitted that the price for accepting waste FRP is higher than that for treating them.

(2) Crystallized glass

Crystallized glass can be recycled as tiles after taking processes of residue powdering, pressing its powder in the tile mold followed by steady baking.[13] Evaluation including its cost by both users and the makers is needed and its practical potential for industrialization has not been studied yet.

2.2.2 Recycling glass fiber in the same state of fiber

Recycling glass fiber in the same state of fiber has been studied for using as reinforcement and insulating materials.

(1) Reinforcement

Char on the surface of glass fiber is cleaned off first followed by surface treating in order to recycle the recovered fiber glass for reinforcement use.[13] Whether to recycle or not depends on the residual strength of glass fiber in this case. Its mechanical strength becomes noticeably weaker as higher treating temperature is applied[18]. Therefore, it is key-issue for possible recycling that the upper limiting temperature for thermal treating is below 200 ℃. The thermal decomposing temperature is usually about 350 ℃ and that of incineration is over 800 ℃ with the result that the mechanical strength of glass fiber is weakened to the point where it cannot be recycled as glass fiber. This method is not promising.

(2) Insulating materials

Fiber is processed without cleaning off char on it for the use of insulating material. This fiber cannot be aimed at high grade insulating materials, but low grade ones are already on the market. The survival of this system depends on its competitiveness with low grade insulating materials from waste glass fiber in its industry. Insulation performance of glass fiber when partly mixed with Calciumcarbonate is not known.

2.2.3 Recycling of glass fiber with some treatments

This is a recycling method to use glass fiber as absorbing materials after applying various treatments. It is currently considered to be the best possible way for using glass fiber and the research and development efforts are primarily focused on these projects.

(1) Porosity processing

Residues are treated with acid to form porous (micro pores) on their surfaces and use as adsorbing materials.[13] A program studying this technology is now underway. The influence of residual paint, adhesives and Calciumcarbonate will be examined by the future studies.

(2) Zeolite processing

By the thermal treatment of powdered glass fiber, zeolite material can be synthesized to be reused as an absorbing material.[19] The formation of zeolite needs the higher technology including selection of raw materials, composition, synthesizing conditions and processing combinations. Today, the product by this method is expected to be a substitute for very valuable natural zeolite being used in cosmetics, fertilizers, soil improving materials and so on. The technical problems are, at present, solved successfully and the products are going to be in cost competitive situation.

(3) Melting and solidifying

To prevent heavy metals in incineration ash from dissolving and diffusing, the ash is melted at higher temperature of 1500 ℃ and is cooled down to be solidified to seal in those heavy metals. This solid can be reclaimed or reused (as tile or aggregates) and this system has been used to some extent by the local municipalities. Glass fiber is the main component of incineration residue in case of FRP. The glass fiber melts at higher temperature than the the melting point of about 830 ℃. It is reported[8] that porosity density can be controlled by melting temperature and cooling down velocity. The existence of porosity can be expected to work as the absorbing material and the filtering material, but this program of studies has just started. The movable disposing system for waste FRP boats[20] was built in November, 1994 (Heisei 5) sponsored by Japan Marine Recreation Association. Pleasure boats themselves can be thermally decomposed at 500 ℃ (dry distillation) without any dismantling in the system. The residues are then melted at 900 ℃ and cooled down to be solidified into stone blocks with much void content. Even if these stone blocks can not be used as filtering materials, it is a feature of completely non polluting process to utilize them in the construction of rivers and roads.[20]

(4) Others

The residues containing more than 50% of SiO_2 can be recycled as raw materials for cement because elements consisting glass fiber do not change substantially through incineration and thermal decomposition.[7] As for the residues, the studies on applications for using asphalt modifier or glass beads are going on.

Appendix 2. Polluting and hazardous material generation by thermal decomposition

The thermal decomposition and incineration have basically similar problems from the secondary pollution point of view. However, there are some different points observed between those two methods because of the presence of Oxygen (no Oxygen in thermal decomposition) and of treating temperature (at lower temperature in thermal decomposition). In general, the thermal decomposition has some bad odor, but it can be said that this system is rather low polluting type because of the advantages in relatively smaller exhausting amount of HCl and NOx in its exhausting gas. The characteristics of polluting and hazardous substances generated through the thermal decomposition are described as follows compared with those of incineration.

(1) Exhausting gas

Considering the air environmental pollution by exhausting gases, the amount of flying dust, NOx, SOx, HCl, dioxin and Styrene gas (cause of bad odor) which are controlled in these permitted exhausting concentrations. Controlling values and total exhausting gas amount are varied with location. Health threatening substances in the air are also oxidized sulfuric compounds, CO, oxidized Nitrogen compounds, Hydrocarbon and flying dust and so forth. An analytical study on the exhausted gas composition during FRP combustion was made using FRP material (unsaturated Polyester resin and glass fiber) of boats experimentally by a small sized electric furnace and by a fluid-bed type furnace. It was found that the amount of individual components exhausted were under the controlling values.[21]

① Exhausting amount

The exhausting amount is smaller than that in incineration. In this system, for instance, when the combustion is made during the final process, it is almost gas phase combustion with less air supplying. Therefore, the total gas exhausted becomes smaller.

② HCl

When Polyvinylchloride is thermally decomposed, HCl gas is generated. This HCl is, however, easily eliminated by an exhausting gas treating equipment as shown in the Guide Line published by the Ministry of Health and Welfare in 1990.

③ Dioxin

This very toxic substance is generated by some chemical reaction of Chlorine containing compounds and some pre-burning substances under existence of Oxygen occurring at around 300 ℃. Therefore, it is quite necessary to take care in handling in the thermal decomposition of Chlorine containing materials.

④ NOx

The thermal NOx is not generated in the thermal decomposition because of its lower reaction temperature. This reaction also occurs in the reduction of atmosphere in chemical and the phenolic NOx generation is also inhibited. Therefore, the thermal decomposition has fewer problems than incineration as far as NOx is concerned.

⑤ Flying dusts

In case of thermal decomposition with FRP, glass fibers fly out to be taken care of after the resin portion is totally decomposed.

(2) Toxic materials

Toxic materials such as Hg, Cd, Pb, organic phosphoric compounds, Cr^{+6} and Zn are regulated in their dissolving concentration. It was reported in the paper that dissolving amount of toxic heavy metals were sufficiently smaller than the controlling value in the fluid-bed type furnace experiment of boat FRP combustion[21]. In case of thermal decomposition, even if Cr is contained in waste material, generation of Cr^{+6} can be inhibited by the thermal decomposing processing.

(3) Bad odor

The substances causing bad odor are burned completely at higher temperature than 700～800 ℃ in general. Accordingly, bad odor problems occur in the thermal decomposition rather than in incineration. Styrene gas, which is the main causes of bad odor during combustion of FRP boats, can be burned completely at 800 ℃ or higher, while the gas is generated at 600 ℃ or lower.[21] There occurs no problem with its higher temperature incineration. However, the thermal decomposition causes the problem when it is usually operated at 500 ℃ or lower.