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A study on manufacturing of a high quality adsorbent using ligneous material as its precursor

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Study on the use of timber heartwood and sawdust by products of wood workings well as small diameter wood and other materials, we have conducted research into the production of high quality adsorbents wide range of the precursor specimens was the used for this research. These specimens included Hokkaido, Akita and Tropical woods. After specimens were prepared and carbonization, activation tests were conducted. Subsequently, adsorption evaluation test was performed. The ash content of the ligneous materials investigated this time was 1% or less and material produced from activation was 3% or less. Excellent results were obtained from the evaluation of adsorbent tests, with the internal surface area reaching 1, 350m^2g and methylene blue adsorbability rising as high as 240mg/g. Based on these results, we brought equipment business scale to install on-site in the Republic of the Philippines and conducted production and performance evaluation test at JICA project (F/S). Estimate for product resulted in almost same level with the fundamental research. We report that we get the opportunity to do research in form laboratory scale of fundamental research to business scale.

Key word: ligneous materials, tropical woods, carbonization, activation, and high quality adsorbents

PROGRESS

Development of and research into high quality adsorbents with coal, petroleum, wood and synthetic high polymer material precursors have been conducted jointly with research institutes within and outside of Japan for many years.

This paper only covers ligneous material. At the start of the study, a carbonization test was conducted by placing samples in the porcelain boat of a horizontal electric furnace.

Because we had experience of conducting production tests of Coalite, we shifted to research on adsorbents. In the same way as for Coalite, a carbonized product was prepared in a porcelain boat. Then some of the material was subjected to a surface diffusion reaction with superheated steam.

Basic research started with activation reaction tests, while the past literature on activation reaction was studied. At a later stage, however, it became necessary to secure some samples in order to confirm the different types of performance under the same conditions, because we were short of samples for of physical adsorption they produced a fluidized bed activation test device using a quartz tube and, as a result, could for the first time produce an activated product with an internal surface area of 1, 380 to 1, 400 m^2/g [1,2,5], which we had never before seen in activation tests of coal produced in Hokkaido. After that, because of the necessity of higher added value of sawdust and mills ends discharged from wood product plants, several companies within and outside the prefecture asked us for technical guidance and to conduct joint research. Because it was easy to achieve 1, 350 m^2/g [2,3,4,5,6] or larger internal surface area repeatedly by the steam gas activation method using ligneous material, many companies showed interest and there was a rush of requests for technical guidance, commissioned and joint research. One of such requests was for commissioned research on high degree application of sawdust (softwood)[5] discharged from a processing plant of imported wood. To compare activation reaction tests by the same method based on the above-mentioned research results, we drew a plan of a quartz reactor tube and had it produced. With the tube, we could prove that it was easy to achieve 1, 350 m^2/g or a larger internal surface area repeatedly.

Because of the low ash, which is a characteristic of wood, remarkable adsorbability was displayed, and it was found that an extremely high adsorbability could be achieved by the gas activation method in the same way as with coal. Because ligneous material would not be corroded during the reaction process in a quartz reaction tube and the activated product does not contain inorganic components, pure products without traces of iron or other substances can be obtained. It was found for the first time, through the research on adsorbents, that the use of quartz reaction tubes would be limited to certain types of coal such as Sunagawa and Anthracite coal because of the large content of inorganic components in coal with many impurities. We were also requested to study the degree of adsorbability which can be achieved by the same processing of mills ends discharged from wood product plants.

As a result of studying samples with a particle size of -2.00 mm in the same way as sawdust, it could be confirmed that the adsorbability of mill ends is comparable to past results.

Problems with activation reaction tests were solved by experimentally producing a stainless steel reaction tube (SUS 316) with an internal diameter of 44 mm and a length of 650 mm and research could be conducted more smoothly. Because the demand for such research from Japanese companies is high, we have always tried to make our research useful for them by taking into account the possibility of scaling up. Based on these research results, many people engaged in wood processing are beginning to think about highly effective utilization of waste.

Also, a survey found that the content of our research corresponded to the needs of low developing countries because the deterioration of forest resources in those countries was becoming a problem at the time.

Under such circumstances, it was predicted that our research theme would be suitable for technical transfer to low developing countries.

Because a survey showed that our research was in line with the policy that should be promoted by low developing countries in the future, we decided to further expand the above mentioned research to promote technical transfer to low developing countries as part of the (Institute for Transfer of Industrial Technology) international industrial technology research project promoted by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

The process of establishing the international industrial technology research project and its details are explained as follows: This project was established in 1973 for systematic use of research institutes of the Agency of Industrial Science and Technology, in order to promote a variety of programs for research cooperation in the mining industry which were in high demand of low developing countries and to contribute to economic development of such countries. Since then, we have made steady progress and improved the content, scale and quality of the project.

The project is currently conducted under joint research with dispatch and invitation of researchers taking priority, based on the economic cooperation expenses provided from the Official Development Assistance (ODA) budget.

Although the establishment of the Institute for Transfer of Industrial Technology as an organization for research collaboration was considered for promoting the project first, the International Research Collaboration Office (present International Research and Development Cooperation Division) was established instead. This project is commonly known as the ITIT project because of this course of events.

A study on manufacturing a high quality adsorbent made from tropical wood. A study was conducted during the five years from 1976 to 1980 on a high quality adsorbents from agricultural and tropical plant waste from the Philippines. Collection and adjustment of materials, thermal analysis, carbonization tests and physical activation tests were conducted to find the properties of the adsorbent.

1. INTRODUCTION

We decided on our official participation in this project for the first time in 1980. Because we had achieved good results in promoting technical guidance, commissioned research and joint research with many companies in Japan, we decided to take an active part in research collaboration in high demand in the mining industry as mentioned above.

We decided to begin a research collaboration project entitled "A study on "Production of High Quality Adsorbents from Tropical Plants" with a national research institute of the Republic of the Philippines.

Both parties agreed on the five-year project from 1976 to 1980 to improve the added value of waste (sawdust, mill ends) produced during wood processing.

2. Preparation of a precursor sample

Ligneous material for the sample precursor was imported from the Philippines and processed into chips.

The prepared sample of -2.00mm pass was dried

for 24 hours at 80℃ with a hot air drier to reduce its water content to approximately 5%, and was stored as the test sample.

3. Thermal analysis

The following types of samples were crushed into -0.074 mm and stored for use in testing and analysis.

3.1. Themogravimetric analysis:

The results of this test give important data for carbonization tests of ligneous precursor samples.

3.2 Proximate analysis

The content of moisture, ash, volatile matter content and fixed carbon was found in accordance with JIS M 8812. The data obtained here are most important for production tests of high-quality adsorbents.

This analysis method is also important for final evaluation because performance values are indicated by it.

4. Carbonization tests

Carbonization tests with a continuous fluidized bed were conducted in this study.

In recent years, however, it has become increasingly difficult to operate this device due to the rapid progress of urbanization around our research institute, and we are obliged to progress with our study using a fixed bed furnace.

5. Activation tests

Out of the samples produced using a fluidized carbonization device, those with a large grain size were crushed into -1.18 to +0.50mm. The samples were separated and activation tests were conducted using a small-scale fluidized bed activation reactor device.

Reaction was induced with heated steam gas as an activator and, after some time, the samples were taken out from the bottom of the device, and the internal surface area and other performance evaluation tests were conducted.

Super heated steam gas was conveyed to the oil bath with a pump (H_2O: 1.00 to 2.50 cm^3/min) that generates and conveys heated steam. A uniform volume of samples (H_2O 1.00cm^3) was used for activation tests at this time.

6. Adsorption evaluation test

6.1. Internal surface area (m^2/g):

By adsorption of nitrogen gas to the adsorbent at the liquid nitrogen temperature, the internal surface area was found from the amount adsorbed by the monolayer of the molecular nitrogen using the BET calculation method.

6.2. Methylene blue adsorbability test (mg/g):

A 300mg/l methylene blue solution was prepared for the adsorption test in accordance with JIS 1474 In this test, an original test method was employed because methylene blue was thought to be important for finding the absolute amount of adsorption and for setting a uniform unit (mg/g) for comparison with the results of iodine adsorbability and other tests.

6.3. Iodine adsorbability test (mg/g):

A solution was prepared in accordance with JIS 1474 The adsorbed amount was indicated by mg/g in the same way as for the adsorbed amount of methylene blue.

6.4. Gas adsorption test (percentage by weight):

The results of tests conducted in accordance with old JIS are shown. Because benzene used for the organic solvent gas adsorption tests was designated as an environmental hormone, JIS K 1474 was partially amended on April 20 1999 after a two year review in accordance with the ISO standards to replace benzene with toluene, acetone and Cyclohexane. Although there were some changes since this study was conducted in 1980 it was thought that there were no significant influences except for those regarding gas adsorption tests.

I. Basic test results were as follows:

We examined a method of producing crushed activated carbon with a fluidized-bed activator using nine types of trees and coconut shell waste (Coir dust) produced in the Philippines. As a result, an internal surface area of 1,000 to 1,500 m^2/g, methylene blue adsorption of 200 to 370 mg/g and iodine adsorption of 900 to 1,200 mg/g were obtained from the product activated under the condition of a carbonization temperature of 420 to 430℃, 10 to 36% yield of carbonized product (dry base) and the activation temperature of 850 ℃. It was therefore recognized that its performance was equivalent to that of commercially available activated carbon.

Although the aforementioned study concerns a production method of crushed and powdered activated carbon, a granulation test was also conducted to expand its uses, taking into account the handling by end users. It is also becoming necessary to use granules to reduce the size of the adsorption device while increasing the amount of carbon to be processed. Based on the above point of view, an internal heat type fluidized bed was produced experimentally for production testing and the study of granular activated carbon to turn it into practical use. As a result, an internal surface area of 1,000 to 1,500 m^2/g, methylene blue adsorption of 200 to 370 mg/g and iodine adsorption of 900 to 1,200 mg/g were obtained from the product activated under the condition of carbonization temperature of 420 to 430℃, 10 to 36% yield of

carbonized product(dry base), activation temperature of 760 to 800, ℃ (internal heat furnace, heated steam, LPG) and 30% yield of activated product (compared with carbonated product). It was therefore confirmed that its performance was equivalent to that have commercially available activated carbon.

At the time of the adsorption performance evaluation test, process evaluation was also conducted concerning the activation time and yield, internal surface area, methylene blue adsorbability, iodine adsorbability, high density and other performances.

To conduct research based on the above results, research teams of the Japan International Cooperation Agency (JICA) were sent to the Republic of Philippines seven times starting in January 1984[10].

II. Subject:

Feasibility Study on the Establishment of the Powdered Activated Carbon Plants in the Republic of Philippines Duration: January 1984 to June 1995. A pilot plant was transported to conduct continuous operation and evaluation tests. At the end of the study, a letter of advice that indicated the feasibility of the plant was submitted to the Philippine government.

Evaluation tests using a practical sized device (carbonization test, continuous activation test and evaluation test of the performance of the product)

III. Summary

A set of activation equipment (gas activation reaction type): A device purchased in Japan was assembled and its parts were inspected before dismantled and transported to the Philippines, where it was reassembled and test operation was conducted.

It was the smallest production scale (20tons/Month) or commercial scale device. This device raises the temperature in the reaction furnace by the reaction of the residual volatile component in the carbonized product and air sent into the reactor, and is thought to be the most suitable type for low developing countries. Figure 1 shows an outline of the activator. Because the temperature control mechanism of the reaction furnace was quite simple controlled by the quantity of carbonized product supply and its maintenance was easy, both the trial operation and final test progressed smoothly.

One set of evaluation equipment: Equipment produced in Japan was purchased and transported to the Philippines, where it was adjusted and used.

Carbonization test device:

Although firebrick and other parts which could not be obtained locally were purchased in and transported from Japan, the furnace was produced and installed by obtaining as many parts as possible in the local area (an open hearth which was low priced and easy to maintain was made and installed experimentally). It was an ideal device for low developing countries, because its structure was simple, maintenance was easy and high quality products could be produced. The open hearth, which is produced in many areas of in Japan from Kyushu to Hokkaido, was used.

Acquisition of sawdust as a sample of precursor for production of an adsorbent. Raw material was acquired by conducting research in Mindanao, Luzon and many other areas of the Philippines.

After conducting research at seven places, material for the following study was purchased from sawmills, which were, located in safe areas and were continuously dealing in wood of homogenous quality. Plants, which were mainly dealing in Lauan near Manila on Luzon and on Mindanao, were selected. It was fortunate that they were very cooperative. Precursors collected from the places mentioned above were used as samples for the study. Verification tests of a variety of conditions were conducted before carbonization and continuous activation tests, while adjusting the evaluation-testing device.

After determining necessary conditions, continuous operation was conducted to prepare for the general plan and the evaluation tests of the product. Preliminary continuous operation for 2 or 3 days was conducted several times using small amounts of several types of samples to warm up the device, give technical instructions to the staff of the local research institute and do related activities. First, one-week continuous operation was conducted to test Lauan sawdust, which is a typical local material, followed by three other continuous tests. The final continuous test was conducted under the best conditions. After repeated discussions on the general conditions to decide if the process and design of this study was suitable for the local situation, a report of the final evaluation and analysis was prepared and submitted to the Philippine government. Fortunately, the device seemed to be ideal for low developing countries because it generated activation reaction heat by the reaction between the volatile component of the carbonized product and air. Naturally, economic analysis was attached to the report. Although everything went smoothly until the report was submitted to the Philippine government, President Marcos lost power due to political changes and the country fell into a

state of political confusion. Since then, this report has been kept in a storehouse without ever being shown to anyone. Although I have tried to transfer the valuable research results to other low developing countries, it seems that the report will never be read even as my retirement approaches. It was an unforgettable experience that made me realize the importance of political stability. Since then, I have been thinking how I can transfer the research results to politically stable low developing countries in Southeast Asia. Although it might have been a small event, it was a very significant experience for me. Knowing that the expenses for the project were paid by the Japanese taxpayers, I was grateful for an opportunity to present a cooperation project for a low developing country and reported about the JICA project entitled the Feasibility Study on the Establishment of the Powdered Activated Carbon Plants in the Republic of Philippines.

This sample is the highest level material for the production of powdered activated carbon in Japan. I hope that you will also pay attention to the analysis value of inorganic components.

Continuous activation test and its evaluation test results.

The production capacity of the activator used for this study was 20 tons/month, the smallest for commercial scale operation. This activation test device was selected as a yardstick of economic efficiency. The device's operation condition, yield and methylene blue adsorption test data for each material are shown. It was confirmed that the results (values) obtained in this study corresponded to the data obtained by the small fluidized bed activation reaction device used for the basic research. It seemed that ligneous samples used for this study contained small amounts of inorganic components but large amounts of calcium. It was also found that elution and refining were easy when processed with mineral acid. Because of this, the activated carbon can be used for a variety of purposes, such as purification of water, food industries and activated carbon for medical use.

It can be said that the production of activated carbon (powdered, granular) directly indicates the state of economic activities in Japan.

Although I will be happy to help them in any way, activated carbon manufacturers in Japan are in a state of overproduction. It is therefore expected that, if production activities are increased any further, manufacturers may end up going down altogether because the market is very limited. Activities in new fields will be necessary to increase production.

That is all for the presentation was concerning the research until June 1985.

It was a valuable experience for me to have an opportunity to conduct basic study concerning the production of a high quality adsorbent using ligneous materials as its precursor, as well as continuous operation production tests using a medium scale production device. I am deeply grateful to many private citizens who helped me with this project. To this day, I have been hoping to find a low developing country to which the valuable results of this industry government cooperation project can be transferred.

IV. Research for the development of a regional promotion policy: [11]

A case of research in Shimokawa Town, Kamikawa gun and Hokkaido. When the above-mentioned JICA project finished, it was decided to begin the exact same research in Hokkaido with a committee system.

I decided to participate in the project in the hope of contributing to the revitalization of the region.

I took part in the Project for High Degree Application of Conifers Produced in Hokkaido to develop a regional promotion policy. It was a study on high degree application of Abies sachalinensis and Japanese larch lumber from thinning, and started with a field study. To increase their added value, a production test of activated carbon was conducted in the same way as in the JICA project. As a demonstration of ligneous resources produced in Hokkaido softwoods, a technical committee commissioned a manufacturer to conduct production and evaluation tests, as well as evaluation of the total production process, although it was only for a short time. From the test results, it was proved that the performance of the product was equivalent to that of ones in the market. Here, research on materials, distance of markets from the producing areas and the actual needs was conducted in the form of a technical committee. The committee argued that it would be too early to form a business or that it would not be suitable for the region. The project was virtually finished by preparing a report without reaching a conclusion even within the organization, which was to form the main body of the project. Only one good thing about this research project was that carbonized products made from tree bark, branches and other forest waste seemed to have gained some popularity in certain areas, although they are usually regarded as semi manufactured products. This seems to be the current state of the agriculture and forestry industries, although I cannot help

thinking it is surprising that such products are becoming popular with the support of the Regional Law Development country.

I think the establishment of the research union of the Forestry Agency at this time was also a great windfall. Although thinning of both conifers and broadleaf trees is necessary for the revitalization of artificial and natural forests, they are actually left untouched in many parts of Japan due to the cost reduction. It is hard to lead revitalization policies for the forest industry to businesses even though they were promoted throughout the country. I have become fully aware of the fact that there are problems, which can never be solved for some types of businesses, although it has been said that we will surely find a way if the collection and processing technologies of resources can be established. Also, it was a valuable experience for me to know that there was no regional difference and that there was a limit to the realization of higher degree application. I earnestly hope that the data of the above project will be useful someday, knowing that the product has adsorbability completely equivalent to commercially available powdered activated carbon. I have presented the data I collected as a report concerning high degree application of ligneous resources.

However, the completely opposite effect will be produced in the case of activated carbon if branches and bark are mixed, and high degree application cannot be expected. Large amounts of inorganic components are accumulated in the bark to protect the trunk. In particular, if alkaline and alkaline earth metal salt react with a carbonated product at a high temperature (800℃) of heated steam, carbon components will have a catalytic effect to shift to the reaction between hydrogen and carbon monoxide (gasification reaction), and activated carbon will not remain. Because this reaction is a nuisance for the activated carbon industry, I would like to emphasize that the prevention of this reaction will be an important point for each manufacturer in order to survive with their own expertise. I would especially like to emphasize that this report is about the production process mainly with the gas activation reaction, which is different from other production processes. In the process of this project, it was often necessary to select materials and methods suitable for the purpose and, in many cases, I could not help realizing the difficulty of achieving high degree application of ligneous natural resources even though the possibility is quite high. I have learned many things from the study, such as the complex workings of nature. I hope you will notice the analysis values of inorganic components. I hope the research and development achieved by the authors will become necessary sometime in the future.

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