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Overview of Bio-Oil from Sewage Sludge by Direct Thermochemical Liquefaction Technology

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ABSTRACT

Sewage sludge is an unavoidable secondary pollution produced in the process of sewage treatment. At present traditional methods of treating sludge (e.g. landfill, incineration or land application) have some disadvantages and shortages. Direct thermochemical liquefaction of sludge is a new treatment method, which has the advantage of both treatment and energy recovery. Research progress and application prospect of sludge liquefaction technology are widely reported, typical liquefaction process with bio-oil production and its main influencing factors are introduced. Besides, the development of this process is illustrated, and resource and energy recovery of this technology are pointed out to be the tendency of sludge treatment in the future.

Keywords: Bio-Oil; Direct Thermochemical Liquefaction; Sewage Sludge

1. Introduction

The increase in the production of sewage sludge from municipal and industrial wastewater plants draws increasing concern, as it represents a potential risk for human health and the environment. Meanwhile, management of sewage sludge resulting from domestic wastewater treatment processes is a complex and expensive process. By aerobic treatment, 0.5 - 1 kg of activated sludge is produced per kilogram of biological oxygen demand (BOD_5) [1].The sludge resulting from domestic wastewater treatment processes consists of a complex heterogeneous mixture of organic and inorganic materials. The solids typically consist of 60% - 80% organic matters. Organic materials in primary sludge are comprised of 20% - 30% crude protein, 6% - 35% fats and 8% - 15% carbohydrates [2]. Though sewage sludge consists of various valuable materials, it is often disposed of as an undesirable and invaluable substance.

The common disposal processes for sewage sludge are landfill, compost and incineration. In view of economic and environmental evaluation, conventional disposal processes have many disadvantages and shortages. Disposal in landfill is always the most frequently chosen treatment for sewage sludge in EU and the US [3-5], but it requires a lot of space and the soil has to be sealed adequately to prevent the leaching of toxic compounds. Compost can result in the accumulation of harmful components, such as the toxic heavy metals in the soil. Incineration is an effective way to reduce the sludge volume and provide stabilization of organic material in sewage sludge [6]. However, the air emissions from incineration are undesirable and restricted. Therefore, alternative solutions to sludge disposal become more and more urgent.

Sewage sludge is considered as an example of renewable energy resources [7]. Some new technologies such as pyrolysis of sewage sludge are in development. The method of bio-oil producing from sewage sludge has attracted most attention in recent years as a promising alternative technology [8-10]. Generally, there are two methods for bio-oil producing from sludge: low temperature pyrolysis and direct thermochemical liquefaction. The technology of low temperature pyrolysis merely requires normal pressure, however, the sludge which is used needs to be dried, so that the water ratio of dry basis is below 5% [11]. Too much energy will be consumed. Moreover, according to energy balance, specific energy consumption (needed energy on the proess/available energy of bio-oil) is approximately 1, surplus energy is extremely low. The method of direct thermochemical liquefaction occurs in the water. Therefore, there is no need for sludge drying. It is very suitable for the property of sewage sludge whose water ratio is above 95% [12-15]. Nowadays, many researchers have transferred their attention to the technology of sludge direct thermochemical liquefaction.

2. Research Status

The essence of direct thermochemical liquefaction is

pyrolysis, including many complex variation, low molecular decomposition reaction and high molecular polymerization of decomposer and so on: the water-soluble intermediate is produced from sewage sludge in the first place, and then sludge is polymerized and hydrolyzed in the aqueous condition. A majority of organics can be transferred to low molecular oily matters by a series of reactions, such as decomposition, condensation, dehydrogenation and cyclization, the product of heavy oil which is produced is further separated and collected by extracting agent.

In recent years, many countries have gone to focusing on the resource reuse and environment friendly disposal of sewage sludge. For instance, USA, UK, Japan and so on [16] mainly study on thermochemical liquefaction, bio-oil is produced from dewatered sludge under the condition of 300˚C and 10 MPa; German and Canada mainly research on bio-oil produced from dried sludge by thermolysis: dried sludge is heated to 300˚C - 500˚C under the anaerobic condition. Meanwhile, the gas is produced, and then the gas is transferred to oily matter. Due to the high cost in the process of research, the attention is gradually paid on direct thermochemical liquefaction, many following processes occurred, such as with alkaline catalyst, nickel catalyst, organic solvents, reducibility. Direct thermochemical liquefaction is applied relatively early in timber field, as for biomass, whatever sludge or timber, their pyrolysis process is similar. Therefore, the typical processes of direct thermochemical liquefaction of sludge are made use of and developed from the timber's processes.

ITOH [17] took advantage of a treatment apparatus that make 5 t/d dewatered sludge turn 48% organics of sludge into heavy oil, calorific value is 37 - 39 MJ/kg under the condition of 300˚C and 10 MPa. YUTAKA [18] studied the bio-oil yield rate of sludge which could be up to 43.5% in the maximum under the condition of 300˚C, 2 MPa of N_2 pressure and catalyst of Na_2CO_3. SHIN-YA [19] found that the dewatered sludge could be liquified at temperatures of 150˚C - 175˚C, and the viscosity of the liquified sludge could be reduced to concentrated sludge (approximately 98% moisture content). Liquified sludge, which has a high solid concentration, could be transported by pumping through a pipe with the same pressure loss as that of concentrated sludge. Li [20] studied deoxy-liquefaction of sludge to liquid fuel in supercritical ethanol. The results showed that the form of CO and CO_2 was the the main process for oxygen reduction. The reactions of compounds in sludge and free radicals with supercritical ethanol were promoted at higher ratio. The significant increment of bio-oil and residue yield was obtained in excess ethanol as extraction and polymerization process.

3. Main influence Factors

3.1. Sludge Types and Operating Conditions

Due to type of different sludge, bio-oil productivity is also quite different. Charothon [21] disposed of activated sludge, digested sludge and paint sludge by pyrolysis. The bio-oil productivity was respectively 31.4%, 11.0% and 14.0%. It showed that different sludge types resulted in different bio-oil productivity. A. Dominguz [22] showed that undigested raw sludge was propitious to sludge liquefaction, especially for raw primary sludge and raw mixed sludge and its bio-oil productivity was 8%, higher than other types of sludge. Jing-Pei Cao [23] suggested that bio-oil yield mainly depended on the content of crude fat in the sewage sludge.

The operating conditions, such as reaction temperature, residence time and heating rate, have a large impact on the process of direct thermochemical liquefaction. Isabel Fonts found that reaction temperature influenced the bio-oil yield to a great extent. The bio-oil yield didn't change at 300˚C under the condition of non-catalyst and 2 h residence time, but change slightly above 300˚C with catalyst. It suggested that bio-oil was mainly produced at 300˚C, and bio-oil productivity increased with the residence time, but slight influence with higher temperature. Senchi [24] studied that heating rate played an important role on bio-oil yield only under the condition of lower temerpature (450˚C, for instance), While heating rate's influence could be ignored at higher pyrolysis temperature (650˚C, for instance); it can be observed that, at 450˚C, high heating rate, pyrolysis efficiency was improved, oppositely solid residua decreased.

3.2. Catalyst

Thipkhunthod [25] found out that catalyst could increase the yield and quality of liquid fuels, improve the pyrolysis efficiency and reduce the cost of craft. Doshi [26] suggested that catalyst' usage could reduce pyrolysis time and reaction temperature, improve pyrolysis ability and decrease solid residua, so that it could get control of the distribution range of pyrolysis products. Shie and Lin [27] had investigated the pyrolysis of sewage sludge with the sodium and potassium compounds catalysts from 377˚C to 467˚C, the results showed pyrolysis conversion rate was improved and arrived the maximum with the catalyst K_2CO_3. Shin-ya Yokoyama [28] found that the usage amount of catalysts influenced the oil yield greatly; when the usage amount of catalysts was 5% of sludge quantity, the most oil yield was up to 48% which was approximately 2 times than that at 20% of sludge quality. But the yield was extremely low with non-catalysts (19.5%).

4. Existing Problems

Compared with western countries' technologies, oil producing from sewage sludge by thermochemical liquefaction technology has just got started in China. The major characteristics of thermochemical liquefaction are that the reaction happens in the water and there is no need for raw materials drying, therefore, this method is extremely suitable for high water ratio biomass. It can be deduced that the method of thermochemical liquefaction will become a development trend of sludge oilation. However, we must reckon with some problems which occur on the process of oil producing from sewage sludge by thermochemical liquefaction:

1) There is surplus 2% - 3% of N_2 in the products of direct thermochemical liquefaction [29-31]. Besides, NO_x that can pollute the air is also produced on the process of liquefaction [32]. So we should take the corresponding measures to get control of it.

2) The operating apparatus is a little bit complexed. Synthetic gases for pressurization is used in some processes in western countries. If the operating pressure increases to spontaneous pressure automatically with water's temperature rising, it will become convenient [33-35]. Consequently, we should take fully into account the types of temperature rising so that the operating will be simple and practicable.

3) There are a wide range of sewage sludge. Apart from domestic sludge, some industrial sludges contain a high content of organic matters. For instance, the content of organic matter of tannery sludge can be up to 70% so that tannery sludge can be seen as a suitable raw material for oil producing from sewage sludge [36]. However, different kinds of sludge always own different kinds of salts of alkaline heavy metals. It is indispensable to fully consider whether these salts of alkaline heavy metals have a catalytic impact.

4) Catalysts influence needs to be further researched. The essence of water thermochemical is pyrolysis, following with many kinds of complex variation, such as low molecule's decomposition reaction, high molecule decomposers' polymerization and so on. Sludge is transferred to water-soluble intermediates in the first place, and then hydrolyzation and polymerization happen again and again in the water. As a consequence, on the process of oil producing from sewage sludge by liquefaction, moderate polymerization is dominating, restraining the polymerization that turns oil into char is more important while catalysts paly an important role. The majority of raw materials chosen for oil producing from biomass by pyrolysis are timbers and catalysts chosen are salts of alkaline metals, such as Na_2CO, K_2CO_3, Al_2CO_3, salts of transitional metals, such as nickel catalyst. But as for their catalystic activities, they need to be further studied. If various kinds and amounts of catalyst are added into the sludge, dynamical model of pyrolysis is established by TGA (thermogravimetric analysis). According to activation energy and frequency factor obtained from thermal degradation kinetic equations and research on various kinds of catalyst's influence on thermochemical liquefaction, we can calculate whether catalysts can play a necessary impact on catalytic oxidation and restrainig polymerization. Based on yield coefficient and products' distribution, we can find out the effective catalyst which can realize the highest rate of oil production.

To sum up, the research directions are to fix these problems and further study these factors' influence on sludge oilation and regular patterns.

5. Concluding Remarks and Outlook

Compared with other methods of sludge treatment, the method of oil producing from sewage sludge, especially direct thermochemical liquefaction, which is a new and green technology corresponding to the development of the times in recent years, owns some necessary advantages. The volume of solid residue decreases greatly; heavy metals existing in the solid residue could resist natural lixivation to a certain extent; reaction temperature needed is lower than incineration so that it could restrict some pollutants' discharge value, such as SO_2, NO_x, dioxin in the pyrolysis gases. The experimental apparatus of direct thermochemical liquefaction is rather simple. Moreover, the aliphatic compounds and proteins of sludge can be transferred to bio-oil, char, gas, and water by low temperature thermochemical reaction. And this kind of bio-oil can be used on-site generated power and fuel for sale.

However, the research of thermochemical liquefaction has just started in China. There is no need for raw materials drying, as a result, only 70% of bio-oil yield was used to meet energy consumption in the process, 30% of bio-oil yield is surplus to be recovered. From this, it can be seen that thermochemical liquefaction will become a competent technology for oil producing from sewage sludge eventually.

Nowadays, many corresponding studies is still at experimental research phase. In economic terms, this method doesn't have the necessary advantages comparead with fossil energy. From the point of sustainable development and environmental protection, this technology owns great developmental potential. To increase competitiveness with primary energy, the liquefaction process must be optimized and operating cost needs to be decreased. In a word, the method of oil producing from sewage sludge by thermochemical liquefaction is a new pathway to solve the sewage sludge issues, and it has broad application prospect.

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REFERENCES

[1] T. R. Bridle, "Control of Heavy Metals and Organochlorines Using the Oil from Seage Process," *Water Science and Technology*, Vol. 22, No. 12, 1990, pp. 249-258.

[2] Y. Kim and W. Parker, "A Technical and Economic Evaluation of the Pyrolysis of Sewage Sludge for Production of Bio-Oil," *Bioresource Technology*, Vol. 99, No. 5, 2008, pp. 1409-1416. doi:10.1016/j.biortech.2007.01.056

[3] E. Pokorna, N. Postelmans, P. Jenicek, *et al*., "Study of Bio-Oils and Solids from Flash Pyrolysis of Sewage Sludges," *Fuel*, Vol. 88, No. 8, 2009, pp. 1344-1350. doi:10.1016/j.fuel.2009.02.020

[4] P. Thipkhunthod, V. Meeyoo, P. Rangsunvigit, *et al*., "Describing Sewage Sludge Pyrolysis Kinetics by a Combination of Biomass Fractions Decomposition," *Journal of Analytical and Applied Pyrolysis*," Vol. 79, No. 1-2, 2007, pp. 78-85. doi:10.1016/j.jaap.2006.10.005

[5] X. R. Jia, B. S. Jin and R. Li, "Fast Pyrolysis of Sewage Sludge in a Fluidized Bed for Oil from Sludge," *Journal of Combustion Science and Technology*, Vol. 15, No. 6, 2009, pp. 528-534.

[6] H. J. Park and H. S. Heo, Young-Kwon Park, *et al*., "Clean Bio-Oil Production from Fast Pyrolysis of Sewage Sludge: Effects of Reaction Conditions and Metal Oxide Catalysts," *Bioresource Technology*, Vol. 101, No. Supplement 1, 2010, pp. S83-S85. doi:10.1016/j.biortech.2009.06.103

[7] C. Jindarom and V. Meeyoo, T. Rirksomboon, *et al*., "Thermochemical Decomposition of Sewage Sludge in CO_2 and N_2 Atmosphere," *Chemosphere*, Vol. 67, No. 8, 2007, pp. 1477-1484.

[8] J.-P. Cao, X.-Y. Zhao, K. Morishita, *et al*., "Fractionation and Identification of Organic Nitrogen Species from Bio-Oil Produced by Fast Pyrolysis of Sewage Sludge," *Bioresource Technology*, Vol. 101, No. 19, 2010, pp. 7648-7652. doi:10.1016/j.biortech.2010.04.073

[9] Q. Y. Shi, B. Li and Y. C. Zhou, "Influence Factors of the Low-Temperature Pyrolysis Process for Oil Production of Sewage Sludge," *Environmental Sanitation Engineering*, Vol. 14, No. 5, 2006, pp. 4-6.

[10] A. X. Pei, L. J. Guo and H. Jin, "Experimental Research on Catalysts and Their Catalytic Mechanism for Hydrogen Production by Gasification of Peanut Shell in Supercritical Water," *Journal of Xi'an Jiaotong University*, Vol. 40, No. 11, 2006, pp. 1263-1267.

[11] A. Dominguz, Y. Fernandez, B. Fidalgo, *et al*., "Bio-Syngas Production With Low Concentrations of CO_2 and CH_4 from Microwave-Induced Pyrolysis of Wet and Dried Sewage Sludge," *Chemosphere*, Vol. 70, No. 3, 2008, pp. 397-403. doi:10.1016/j.chemosphere.2007.06.075

[12] X. Z. Yuan, H. J. Huang and G. M. Zeng, "Total Concentrations and Chemical Speciation of Heavy Metals in Liquefaction Residues of Sewage Sludge," *Bioresource Technology*, Vol. 102, No. 5, 2011, pp. 4104-4100.

[13] G. F. Gong, M. Y. Zhang, Y. D. Huang, *et al*., "The Experimental Research on Liquefaction of Lignocellulose in Sub-Critical and Supercritical Water," *Applied Chemical Industry*, Vol. 37, No. 11, 2008, pp. 1275-1280.

[14] E. Gasafi, M.-Y. Reinecke, A. Kruse, *et al*., "Economic Analysis of Sewage Sludge Gasification in Supercritical Water for Hydrogen Production," *Biomass and Bioenergy*, Vol. 32, No. 12, 2008, pp. 1085-1096. doi:10.1016/j.biombioe.2008.02.021

[15] A. Dominguez, J. A. Menednez and J. J. Pis, "Hydrogen Rich Fuel Gas Production from the Pyrolysis of Wet Sewage Sludge at High Temperature," *Journal of Analytical and Applied Pyrolysis*, Vol. 77, No. 2, 2006, pp. 127- 132. doi:10.1016/j.jaap.2006.02.003

[16] I. Fonts, M. Azuara, G. Gea, *et al*., "Study of the Pyrolysis Liquids Obtained from Different Sewage Sludge," *Journal of Analytical and Applied Pyrolysis*, Vol. 85, No. 1-2, 2009, pp. 184-191. doi:10.1016/j.jaap.2008.11.003

[17] S. itoh, *et al*., "Production of Heavy Oil from Sewage Sludge by Direct Thermochemical Liquefaction," *Desalination*, Vol. 98, No. 1-3, 1994, pp. 127-133.

[18] D. Yutaka, *et al*., "Studies on the Direct Liquefaction of Protein-Contained Biomass: The Distribution of Nitrogen in the Productions," *Biomass and Bioenergy*, Vol. 11, No. 6, 1996, pp. 491-498.

[19] S.-Y. Yokoyama, *et al*., "Thermochemical Liquefaction of Dewatered Sewage Sluge," *Biomass and Bioenergy*, Vol. 4, No. 4, 1993, pp. 243-248. doi:10.1016/0961-9534(93)90081-E

[20] H. Li, X. Z. Yuan, G. M. Zeng, *et al*., "The Formation of Bio-Oil from Sludge by Deoxy-Liquefaction in Supercritical Ethanol," *Bioresource Technology*, Vol. 101, No. 8, 2010, pp. 2960-2866.

[21] C. Jindarom, V. Meeyoo, T. Rirksomboon, *et al*., "Thermochemical Decomposition of Sewage Sludge in CO_2 and N_2 Atmosphere," *Chemosphere*, Vol. 67, No. 8, 2007, pp. 1477-1484.

[22] A. Dominguz, Y. Fernandez, B. Fidalgo, *et al*., "Bio-Syngas Production with Low Concentrations of Co_2 and CH_4 from Microwave-Induced Pyrolysis of Wet and Dried Sewage Sludge," *Chemosphere*, Vol. 70, No. 3, 2008, pp. 397-403. doi:10.1016/j.chemosphere.2007.06.075

[23] J.-P. Cao, X.-Y. Zhao, K. Morishita, *et al*., "Fractionation and Identification of Organic Nitrogen Species from Bio-Oil Produced by Fast Pyrolysis of Sewage Sludge," *Bioresource Technology*, Vol. 101, No. 19, 2010, pp. 7648-7652. doi:10.1016/j.biortech.2010.04.073

[24] S. Inoue and S. sawayama, "Behaviour of Nitrogen during Liquefaction of Dewatered Sewage Sludge," *Biomass and Energy*, Vol. 12, No. 6, 1997, pp. 473-475.

[25] V. A. Doshi, H. B. Vuthaluru and T. Bastow, "Investigations into the Control of Odour and Ivscosity of Biomass Oil Derived from Pyrolysis of Sewage Sludge," *Fuel Processing Technology*, Vol. 86, No. 8, 2005, pp. 885- 897. doi:10.1016/j.fuproc.2004.10.001

[26] J. L. Shie, J. P. Lin, C. Y. Chang, *et al*., "Pyrolysis of Oil Sludge with Additives of Sodium and Potassium Compounds," *Resources, conservation and recycling*, Vol. 39, No. 1, 2003, pp. 51-64. doi:10.1016/S0921-3449(02)00120-9

[27] S.-Y. Yokoyama and A. Suzuki, "Oil Production from Sewage Sludge by Direct Thermochemical Liquefaction," *Trends in Physical Chemistry*, Vol. 40, No. 1, 2003, pp. 157- 165.

[28] H. J. Park, H. S. Heo, Y.-K. Park, *et al*., "Clean Bio-Oil Production from Fast Pyrolysis of Sewage Sludge: Effects of Reaction Conditions and Metal Oxide Catalysts," *Bioresource Technology*, Vol. 101, No. 1, 2010, pp. S83-S85. doi:10.1016/j.biortech.2009.06.103

[29] H. J. Huang, X. Z. Yuan, G. M. Zeng, *et al*., "Thermochemical Liquefaction Characteristics of Sewage Sludge in The Sub- and Supercritical Acetone," *China Environmental Science*, Vol. 30, No. 2, 2010, pp. 197-203.

[30] R. Zhao, D. Liu, Q. B. Li, *et al*., "Prospect Discussion on Sludge Energy Utilization," *Journal of Anhui Agricultural Sciences*, Vol. 36, No. 14, 2008, pp. 6004-6007, 6016.

[31] X. Y. Ren, J. M. Chang, J. S. Gou, *et al*., "Research and Development Trends of Direct Liquefaction of Wood Biomass," *World Forestry Research*, Vol. 22, No. 5, 2009, pp. 62-65.

[32] L. J. Guo, Y. J. Lu, X. M. Zhang, *et al*., "Hydrogen Production by Biomass Gasification in Supercritical Water: A Systematic Experimental and Analytical Study," *Catalysis Today*, Vol. 129, No. 3-4, 2007, pp. 275-286.

[33] S.-Q. Zhang, X.-Mi. Yue, Z.-Y. Yin, *et al*., "Study of the Co-Pyrolysis Behavior of Sewage-Sludge/Rice-Straw and the Kinetics," *Procedia Earth and Planetary Science*, Vol. 1, No. 1, 2009, pp. 661-666.

[34] G. Gasco, M. J. Cueto and A. Mendez, "The Effect of Acid Treatment on the Pyrolysis Behavior of Sewage Sludges," *Journal of Analytical and Applied Pyrolysis*, Vol. 80, No. 2, 2007, pp. 496-501. doi:10.1016/j.jaap.2007.03.009

[35] J. Chuimpoo and P. Prasassarakich, "Bio-Oil from Hydro-Liquefaction of Bagasse in Supercritical Ethanol," *Energy & Fuels*, Vol. 24, No. 3, 2010, pp. 2071-2077. doi:10.1021/ef901241e

[36] L. H. Zhang, C. B. Xu and P. Champagne, "Overview of Recent Advances in Thermo-Chemical Conversion of Biomass," *Energy Conversion and Management*, Vol. 51, No. 10, 2010, pp. 969-982.

