

Disposal of Solid Wastes from the Paper Industry Using a CHTC-based Technology: A Preliminary Study

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【 Summary 】

The domestic paper industry is using tremendous amounts of recycled wastepaper as raw material for papermaking. Fair amounts of external matter get into the system along with the wastepaper and end up as various solid wastes. Biological treatment of mill effluents also produces large amounts of sludge. Disposal of the solid wastes presents an onerous task for the industry. Thus, we tried the catalytic hydrothermal conversion (CHTC) technology using alkali salt (Na_2CO_3) to catalyze the formation of hydrogen and carbon monoxide at mid-temperature ($< 800^\circ\text{C}$) and atmospheric pressure. The process might be a viable technique for disposing of organic solid wastes and recovering the energy contained therein, thereby effectively reducing the volume. In trial process, rejects from wastepaper-based paper mills and their sludge were tested. Sericite (a mica mineral) was found to facilitate heat transfer and enable good conversion efficiencies. In the first series, reacted ashes had less than 5% volatile substances, indicating effective volume reduction, even with the passive mode of reaction (no steam injection or agitation) and more than 40% hydrogen emissions in the flue gas. Overall we deemed the process viable, but reactor design must enable good mixing and high-temperature steam injection to arrive at the potential optimal reaction conditions.

Key words: CHTC (catalytic hydrothermal conversion), solid wastes, disposal, energy recovery, volume reduction.

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研究報告

紙業固體廢棄物催化劑濕熱轉化研究之初探

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摘要

台灣造紙工業高度仰賴廢紙為原料，廢紙中的夾雜物以及廢水生物處理產生之污泥處置遂為紙業一大負擔。本研究嘗試以催化劑濕熱轉化(CHTC)技術，即利用鹼金屬鹽於中溫(< 800°C)下將含水試材/注入高壓蒸汽催化產氫反應，並轉化有機碳為一氧化碳，或為可行之方案以處置有機固體廢棄物，回收其中能源並達有效減容之目的。桌上型反應器測試廢紙再生廠之製程排渣與生物污泥之處理。試驗發現添加絹雲母可改善熱傳導及強化轉化反應。系列反應結果，在無蒸汽注入情況下，產生之灰渣含揮發性物質低於5%，而產氣中含氫量常超過40%。整體評估，本法應用於處置紙業廢棄物有其可行性，惟須先克服熱傳導與蒸汽有效注入之技術以達到潛在之最適反應條件。

關鍵詞：催化劑濕熱轉化、固體廢棄物、處置法、回收能量、減容。

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INTRODUCTION

The paper industry in Taiwan is heavily dependent on the resources of wastepaper, realizing a utilization rate of about 75% and a recovery rate of 60%, both figures rank high among countries of the world (TPIA 2004). Despite the success of basing a viable industry largely on recycled resources, which has numerous positive connotations for the economy and environment, such as reducing wastes, lowering carbon dioxide emissions, extending life cycles of products, maximizing marginal benefits, etc., there are associated downsides and pitfalls as well.

One concern is that domestic recovered wastepaper, which reaches nearly 3 million metric tons annually, is composed of about 10~15% of contraries, i.e., materials mixed in with the wastepaper that are useless or harmful to the papermaking process or quality of the products. These materials are in a true sense, the various kinds of trash from people's

daily lives, discarded and mixed in with the recycled waste paper and boards. Some of the heavier contraries, such as metals, glass, stones, sand, and the like relatively easily separate from the pulp stock using differences in specific gravities; whereas certain light weight entrained substances often cause various problems. Thus the secondary fiber processes often consist of various separation measures such as screening, cyclone cleaning, flotation, and washing to achieve separation of the contraries. Eventually, the waste materials from the process end up as process rejects, including various contraries; or biosludge from secondary treatment of wastewater streams. These are solid wastes of the paper industry that need to be disposed of as "industrial wastes."

Traditional methods of disposing of solid wastes include sanitary landfilling, incineration, composting, and land application of

treated sludge. Many of the traditional options are costly or untenable due to restrictions on available land, and environmental impacts. Thus novel treatment methods need to be explored. Among these, wet-oxidation processes have been touted, but these processes require very high pressures, often exceeding 200 bars, thus they could pose insurmountable technical limitations for routine disposal.

The catalytic hydrothermal conversion (CHTC) technology can effectively convert all organic materials through reaction with water vapor at a mid-high temperature range of less than 800°C and minimal pressurization. After careful evaluation, we deemed that this process has good potential to resolve the solid waste disposal problem. The process was pioneered and put to limited practical application during the first Gulf War in the early 1990s. American encampments shunned any contact with local civilians, thus they relied on the CHTC process units to dispose of their wastes.

MATERIALS AND METHODS

Materials

Solid wastes from several sources were collected, including sludges from secondary treatment of an old corrugated containerboard (OCC) mill, an integrated pulp and paper mill, and process rejects from an OCC mill pulper; a whiteboard mill pulper, and stock preparation system; as well as some fibrous rejects from a specialty paper mill. In addition, some wood wastes from the wood-based industry, particularly sawmills, were also collected for this study.

All solid wastes were stored in airtight plastic bags for transportation. Once back to the lab, the moisture content, total carbon, heat value, and ash content of the materials were analyzed (Tables 1, and 2).

The various solid wastes were spread out and air-dried. Then these were broken down in a Wiley mill into finer particle sizes. After processing, the moisture contents were again

Table 1. Compositions of mill residues from the local pulp and paper industry

Mill category	Solid waste	Moisture content (%)	Ash (%)	Heat value (cal/g)
Whiteboard	Sludge	76.1	40.0	2381.8
Whiteboard	Stock prep. rejects	69.5	22.5	3481.9
Whiteboard	Pulper rejects	61.9	4.7	---
OCC to medium	Sludge	72.3	59.2	1851.3
OCC to medium	Pulper rejects	50.9	6.5	---
Specialty paper	Fibrous resid.	86.3	18.1	3073.0
Integrated mill	Proc. rejects	26.5	36.1	---

Table 2. Ash and condensate characteristics of the preliminary CHTC trials with the addition of high amounts of catalyst/absorbent (heat transfer medium)

Solid waste	Inorganic ash (%)	Condensate pH	Condensate TS (mg/L)	Condensate COD (mg/L)	Cond. (mS/cm)	Turb. (NTU)
Sludge	95.5	8.05	30	456	3.48	219
Process rejects	95.7	7.52	1100	486	1.92	147

Cond: conductivity; Turb: turbidity; TS: Total solids; COD: chemical oxygen demand.

analyzed, and the samples stored in a cold room prior to CHTC treatment.

Methods

A bench-top CHTC reactor was assembled based on a blueprint supplied to us by Applied Research Associates (ARA), Panama City, FL, USA., our technical advisors and overseas cooperative research partners (Li and Renard 2001). Due to the lack of suitable manufacturers, the heart of the reactor, a 2.54-cm pitched auger, needed to be ordered from the US. Unintentional mistakes in the selection of the stainless steel caused the first 2 augers to fail.

Finally an S310 high-temperature stainless steel auger was obtained, and the reactor commenced trial operations (Fig. 1). The reactor consisted of a feeder hopper for inputting the solid wastes, a steam heater, and a reactor with an auger rotating at about 1~2 cycles per minute to transport the solid wastes up an incline. The reactor was encased in an electrical heater capable of generating temperatures of about 1000°C, and the gases

evolved from the reactor were directed down a condenser tube and finally to a liquid-gas separator. Thermal couples for sensing and controlling temperature at various points were installed.

When in operation, the reactor was pre-heated to the desired reaction temperature, usually 750°C, and cooling water was turned on. Then for each run, about 20 g oven-dry (o.d.) of the sludge or process rejects was fed into the reactor. Because a steam generator installed near the in-feed hopper was largely ineffective, we found that by simply using a high waste moisture content (70~80%), sufficient steam would passively be generated to allow a reasonable degree of conversion. The catalyst we chose was sodium carbonate. In order to scavenge certain undesirable gases such as hydrochloride, we originally used slaked lime but once the wet lime absorbed carbon dioxide, it formed calcium carbonate, i.e., limestone, and caked up the reactor. Eventually we used sericite (a mica mineral) to help conduct the heat. Sericite is a locally produced mineral of a platy nature, low abra-



(a) Feed hopper; (b) auger motor; (c) reactor casing; (d) heating units and thermocouple connection; (e) ash tube; (f) condenser; (g) cooling water supply; (h) liquid-gas separator; (i) flue gas tubing; and (j) steam generator.

Fig. 1. Photo of the CHTC bench-scale reactor setup.

siveness, and good heat capacity.

The fuel gas from the reactor passed through a filter and a hydrogen detector, which provided the concentration of the hydrogen gas evolved. The gases were flared off afterward. Condensates from the reactor were collected and analyzed for their environmental quality, such as COD, total solids (TS), turbidity, and total carbon (TC).

RESULTS AND DISCUSSION

Characterization of solid wastes

Characteristics of the solid wastes collected from various pulp and paper mills are shown in Table 1. The results indicated that most of the pressed sludges and rejects had a solid content of $\geq 30\%$, with the exception of wetter rejects from a specialty paper mill and the air-dried, lower-moisture fluffy residue of the integrated mill.

Ash contents of the solid wastes varied widely. One peculiar case was the OCC medium mill, which tended to have sludge with a very high ash content (59.2%). Heat values of the solid wastes were dependent upon the organic contents of the wastes. OCC mill sludge, therefore, was generally poor in heat value and probably not well treatable by the process.

Mechanisms of the CHTC

When organic-containing wastes are thermally converted, they turn into a fuel that has higher energy content than the feedstock. Also, the volume and weight of the disposable mass are also significantly reduced. Most such conversion processes aim to produce fuel gas, typically a mixture of carbon monoxide and hydrogen. Thermal conversion of carbon-containing solid wastes involves several gasification and steam-reformation reactions (Buekens and Schoeters 1985):

The Boudouard reaction:



Methane reaction:



Water-gas shift reaction:



Steam-reformation reactions:



Reaction (3) is the most-important steam reformation reaction, often referred to as the water-gas shift reaction. Reaction (5) is also a steam-reformation reaction that produces much heat. The hydrogen-to-CO ratio produced in the conversion is affected by the catalysts used, system temperature, and steam-to-carbon ratio. Adding water is often difficult to control and creates other practical problems. Pyrolysis is especially important in gasification, since its products can consume organic substances in solid wastes, leaving fewer organics to be gasified to the desired gaseous products. Hence catalysts that enhance gasification have been extensively researched to produce greater amounts of gaseous products, in order to minimize tar and char production and control gas compositions. Two classes of catalysts were found to be effective: carbonates of alkaline metals and supported metal catalysts (Fung and Graham 1980). However, catalysts often have short lifetimes. Based on the regeneration capability, alkali carbonates show more promise than metal catalysts. The former has been used as a steam gasification catalyst and was shown to increase both the rate and conversion of carbon to gas. A study using graphite as a substrate found that sodium carbonate enhanced the gasification rate and net gas yields with carbon monoxide as the main end gas component. The catalyst also promoted the water-gas shift reaction when steam was injected (Fung and Graham 1980). Brown et al. (1985) also found that

when using potassium carbonate as a catalyst, the reaction rates at 650°C approximately equaled the non-catalyzed reaction rates at 870°C, and caused a 5-fold increase in the char gasification rate as compared with the non-catalyzed reaction at 750°C. Activated nickel-based catalysts are also effective in promoting gasification. Brown et al. (1985) found that all tar was converted to gas with this catalyst. The catalyzed reforming and cracking reactions effectively reduced the char yield through the thermal decomposition of tars, when wastes were mixed with a catalyst during pyrolysis. Much research has concentrated on the regeneration and deactivation of catalysts. For economic viability, catalysts must be resistant to deactivation or must be easily regenerated (Baker et al. 1985). The CHTC technology received renewed attention during the first Persian Gulf War and has been applied to treat sludge from sewage (Richardson 1997) and biomass (Chonet et al. 1996, Li and Renard 2001).

Initial CHTC trials using high additive contents

In our initial trials of the CHTC reactor, we used very high proportions of the catalyst and absorption/heat-transfer inorganic material (slaked lime) so as to minimize the possibility of a poor reaction due to an insufficient amount of catalyst. Also because the heater for steam generation was ineffectual and the long passage channel for feeding the wastes posed various problems. The configuration of the reactor was modified with the feeder hopper directly attached to the reactor input to facilitate waste input. Air-dried solid wastes were adjusted to 20% solids content, thus there would be sufficient water to produce steam inside the reactor. The tests showed that when sludge and stock preparation rejects from a whiteboard mill were placed in

the reactor maintained at 750°C, combustible gas was emitted and flared off (gas analyzing instruments were still on order then); the ashes and condensates after the reactions had low organic content (Table 2). These proved the feasibility of the treatment. However, the large amounts of lime with wet solids often turned to hard limestone and caked up the reactor.

Table 2 shows that under a condition of catalyst oversupply, most of the organic substances in the wastes were turned into gaseous products. The CHTC process thus is able to achieve reasonably good conversion of the residual organic substances in the wastes into fuel gases.

Trials with sericite as a medium

The adverse situation produced by lime addition led us to exclude it altogether. An alternative for use as the substance medium needed to be found. We tried bentonite, quartz sand, and sericite. Bentonite has a similar caking tendency, quartz sand is too abrasive, so only sericite, a silicate mineral of the mica family with a platy structure, low abrasiveness, and good heat capacity was found to perform satisfactorily. We also reduced the proportions of the medium and catalyst. Results of a series of tests using the same sludge and process waste at 20 g o.d. mass are shown in Table 3. The residual volatile solids generally improved; condensates also tended to have lower COD values. Advantages of using mica included smoother, unperturbed operation and more-predictable results. As the mineral swells in water, it might also help by transporting water up the reactor, which is subsequently converted to steam in the appropriate reaction zone. Results also indicated that the catalyst (sodium carbonate) needs to be added at no more than a 5% level, probably even less to give reasonable conversion

Table 3. Conditions of sericite-mediated CHTC reactions and ash and condensate characteristics

Waste	Mica (g)	Na ₂ CO ₃ (g)	Volatiles in ash (%)	Condensate				
				pH	TS (%)	COD(mg/L)	Turb. (NTU)	TC (mg/L)
Rejects	18	2	2.25	--	--	--	--	--
	13	2	1.51	8.25	0.05	239	40.5	84.9
	13	2	4.10	--	--	--	--	--
	10	1	5.74	8.16	0.07	171	70.1	67.2
Sludge	18	2	2.53	--	--	--	--	--
	9.93	2	1.68	--	--	--	--	--
	15	1	1.20	7.75	0.05	206	46.7	91.2
	10	1	0.75	7.67	0.05	238	40.4	96.2

TS: total solids; COD: chemical oxygen demand; Turb.: turbidity; TC: total carbon.

performance at 750°C.

Flue gas from the reactor was first flared off, with good flammability. When a hydrogen gas analyzer was delivered later, we fed the flue gas into the analyzer and found that the hydrogen concentration fluctuated somewhat. Under a steady state, however, roughly a 40% hydrogen gas concentration was obtained. We presumed that the ratio would be higher if an adequate steam injection apparatus were installed on the reactor. Figures 2 to 4 show the emission of hydrogen with time as

stock preparation rejects and sludge were fed into the reactor using various proportions of catalyst and medium.

Overall, at this stage, we think that the treatment is feasible. Considering the relatively high costs required to dispose of solid wastes, even if the reactions require extra energy inputs, other than that supplied by the fuel gas, the overall ease of pretreatment and recoverability of the catalyst and medium should make this method a potentially practical approach to dispose of paper mill solid wastes.

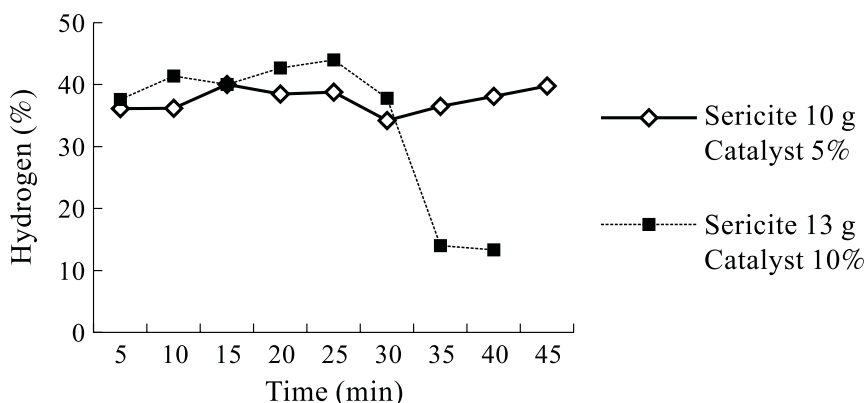


Fig. 2. Hydrogen gas emissions from the process rejects of a whiteboard mill during CHTC reactions.

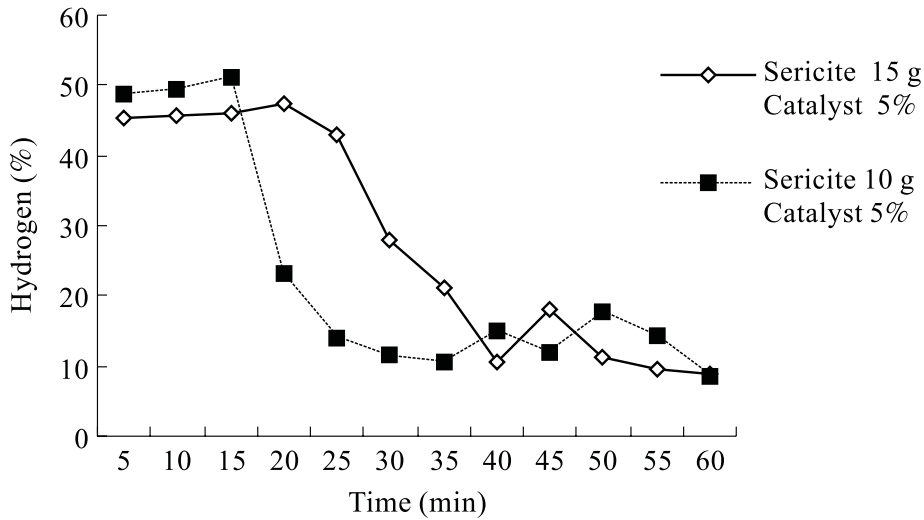


Fig. 3. Hydrogen gas emissions from the sludge of a whiteboard mill during CHTC reactions.

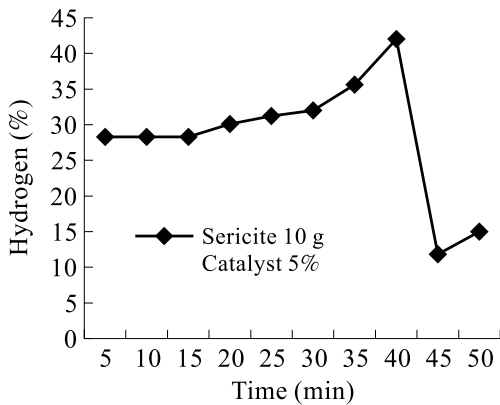


Fig. 4. Hydrogen gas emissions from process rejects of a whiteboard mill during pyrolysis reaction.

CONCLUSIONS

This study has shown that one of the problems facing Taiwan's paper industry, solid waste disposal, can potentially be solved using the catalyst hydrothermal conversion (CHTC) process for treating sludge and organic process rejects. In the CHTC treatment of mill rejects and sludge, we found that the original sequestration medium selected,

calcium oxide/hydroxide, was inappropriate due to formation of a hard calcium carbonate encrustation, which caused the reactor auger to freeze up. Sericite powder of ~14 μm in average size was found to be a good heat conduction medium that enhanced hydrogen gas emission. Overall, the study showed that the approach is fundamentally sound and feasible, even without active steam injection. The prospect of practical application requires further studies and scale-up of treatment facilities.

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LITERATURE CITED

Baker EG, Mudge LK, Wilcox WA. 1985. Catalysis of gas-phase reactions in steam gasification of biomass. In: Overend RP, Milne TA, Mudge LK editors. Fundamentals of thermochemical biomass conversion. New York: Elsevier Applied Science Publishers. p 863-74.

Brown MD, Baker EG., Mudge LK. 1985. Catalysts for biomass gasification. Energy Biomass Waste 9:505-21.

Buekens AG, Schoeters JG. 1985. Modeling of biomass gasification. In: Overend RP, Milne TA, Mudge LK editors. Fundamentals of thermochemical biomass conversion. New York: Elsevier Applied Science Publishers. p 619-89.

Chornet E, Wang D, Czernik S, Montane D, Mann M. 1996. Biomass-to-hydrogen vs. fast pyrolysis and catalytic steam reformation. Proc. 1996 US DOE Hydrogen Program Review. Miami, FL: US DOE. 1996 May 1-2, Vol. 1, NREL/CP430-21968. p 457-80.

Fung DPC, Graham R. 1980. The role of catalysis in wood gasification. In: Jones JL, Radling SB editors. Thermal conversion of solid wastes and biomass. Washington, DC: Am Chem Soc. p 369-78.

Li LX, Renard J. 2001. Personal communications.

Richardson J. 1997. Hydrogen production by gasification of biomass and wastes. Lawrence Livermore National Laboratory. 28 pp.

