

# WET OXIDATION OF MUNICIPAL BIO-SOLIDS IN NEW ZEALAND. AN OVERVIEW

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## **ABSTRACT**

Management and disposal of sludge generated in municipal waste water treatment plants constitute serious logistical and financial problems, in addition to stringent landfilling regulatory requirements. Wet oxidation, a technology invented in the 1950s, was considered as a solids deconstruction method.

The conventional approach of this technology is to target destruction of the organics to carbon dioxide and water. In contrast, this work utilised wet oxidation as a conversion technology, targeting deconstruction of municipal biosolids into valuable compounds such as acetic acid. Laboratory-scale (600 mL) reactor studies were utilised to determine the impact of different process conditions on deconstruction performance. The results obtained indicated that significant yield and purity of acetic acid could be achieved in hydrothermal processes for beneficial re-use. As a result, a joint project with Rotorua District Council to establish a pilot plant to conduct further studies for commercial plant scale design is currently underway.

## **KEYWORDS**

wet oxidation, thermal hydrolysis, solids deconstruction, solids destruction, volatile fatty acids

# 1 INTRODUCTION

The subcritical hydrothermal processes, thermal hydrolysis and wet air oxidation are effective technological solutions for the destruction of solid organic wastes. Thermal hydrolysis, involves the splitting of cells and long chain molecules (lysis) in the presence of water (hydro) by the application of heat (thermal). Typically, operating conditions for thermal hydrolysis are in the range of 140 – 180 °C, 0.6 – 2.5 MPa with no addition of oxidants (Shanableh, 2000, Khalil et al., 2005, Mucha and Zarzycki, 2008). On the other hand, wet air oxidation involves the liquid phase oxidation of organics or oxidizable inorganic components at elevated temperatures (125 – 320 °C) and pressures (0.5-20 MPa) using a gaseous source of oxygen (Mishra et al., 1995). In both processes, it is ensured that the total pressure is kept above the vapour pressure of water to minimise boiling of the bulk liquid and improve the solubility of oxygen (Khan et al., 1999).

Application of thermal hydrolysis has been developed into a number of commercial systems for different applications. For example, CAMBI and Thelys™ are thermal hydrolysis commercial processes developed specifically as a pre-treatment stage to optimise the anaerobic digestion phase by increasing the quality of biodegradable organic matter and hence reducing the size of digester required and enhance biogas production (Belkhodja, 2003). Other applications of thermal hydrolysis aim to convert the sludge to a sterile, biologically stable form which has good settling and dewatering properties (Mishra et al., 1995).

Industrial application of wet oxidation (Kolaczowski et al., 1999, Luck, 1999) has been primarily commercialised as a sludge volume reduction technology with limited emphasis on alternative reaction pathways which can produce useful by – products. The Athos™ Process, a technology successfully commercialised by Veolia Systems (France) achieved > 98% sludge volume reduction and COD removal > 85 % (Belkhodja, 2003).

Lately, it has been realised that the production of high levels of volatile fatty acids (VFAs) as by products of incomplete wet oxidation can be an advantage in BNR waste water plants and as such the renewed interest in the technology (Shanableh,2005). VFAs are readily biodegradable, and therefore provide a potentially valuable carbon source for the biological denitrification process. Several wet oxidation studies (Wu et al., 1999, Khan et al., 1999, Jin et al., 2005, Shanableh.A., 2005, Mucha and Zarzycki, 2008, Chung et al., 2009) have indicated

that acetic acid is the most dominant VFA in thermal treatment of municipal biosolids due to its thermal stability.

A two – stage process has been developed (Jin et al., 2005), targeting production of acetic acid from municipal biosolids. The two – stage process consist of both a hydrolysis process step without oxygen supply subsequently followed by wet oxidation process step, utilising hydrogen peroxide as the oxidant. The authors used hydrogen peroxide, reaction temperatures of 300 °C and carbohydrate-based wastes .Alternatively we investigated the combined effect of thermal hydrolysis and wet oxidation on the conversion of bio-solids, at lower reaction temperatures and using oxygen as the oxidant.

The influence of subcritical hydrothermal treatment of municipal biosolids as a conversion rather than destructive technology was investigated using three processes distinguished by their operating conditions. The three processes were (1) thermal hydrolysis at 140 °C (2) wet oxidation at 220 °C and (3) a two – stage process which acted as a series combination of the processes in (1) and (2), but with a single reaction temperature of 220 °C. A specific hypothesis for testing was that the hydrothermal conversion mechanisms proposed by Jin et al., (2005) would still occur on the bio-solids carbohydrate component at lower temperature of 220°C, resulting in an enhancement in the production of acetic acid for the two-stage process, over that of low temperature thermal hydrolysis and single stage wet oxidation. The performance of the three processes was compared and ultimately considered in view of the potential to separate the carbonaceous compounds for beneficial re-use.

## **2 EXPERIMENTAL SECTION**

### **2.1 MATERIALS**

The sludge used in this study was taken from Rotorua District Council waste water treatment plant in New Zealand. The plant is a high rate activated sludge process based on the BARDENPHO configuration. The sludge which contains about 15 % dry weight solids is belt press filtered prior to despatch to a landfill. The sludge samples were stored in a freezer to protect them from putrefaction and defrosted when required for the experimental work. Owing to its non – homogeneity, the sludge was homogenised and diluted to 2.5 – 3 % solids for the experimental work.

## 2.2 EQUIPMENT

The batch reactor system (Fig. 1) consisted of a high pressure 600 ml reactor (Parr Instruments, USA) made of titanium alloy capable of operating at pressures up to 200 bar and temperatures up to 350 °C. The reactor was equipped with a thermocouple, a single loop water coil, a gas dip tube which extended beneath a two blade impeller and a gas sample withdrawal port located at the reactor head. The impeller was operated at 355 rpm to eliminate the effects of diffusion mass transfer resistance. Pressure was controlled by a backpressure valve regulator and was measured using a pressure transducer. A non-return valve was installed at the gas inlet. The reacting system was also equipped with a bursting pressure valve to vent off in the case of reactor overpressure. The reactor bomb cylinder was placed in a heating mantle, which supplied electrical heat during process heat up. The reactor temperature was controlled by the Parr Instrument reactor controller (Model 4572).

## 2.3 EXPERIMENTAL PROCEDURE

Table 1 shows the experimental conditions applied in this study.

*Table 1 Experimental conditions.*

	Temperature	Pressure	Oxidant	Time
	°C	MPa		mins
Thermal Hydrolysis	140	1	None	120
Wet oxidation	220	1	O <sub>2</sub>	120
Two – stage	220	1	None/O <sub>2</sub>	240

During a typical batch test, the reactor was charged with homogenized 200 ml sludge of known strength (ie, VSS, VFA, COD, TOC, etc). During the thermal hydrolysis experiments, the reactor was pressurised with nitrogen to 1 MPa and the temperature increased to 140 °C. For the wet oxidation experiment, the reactor was pressured at ambient temperature with pure oxygen and the temperature increased to 220 °C. The oxygen pressure was in excess to the stoichiometric chemical oxygen demand requirements calculated using the ideal gas law. In both cases the reactants were allowed to react for 120 minutes after the reaction temperature was achieved. The two – stage experimental work was done in sequence. The first stage involved pressurising the reactor with N<sub>2</sub> to 1

MPa under ambient conditions. The temperature was increased to 220 °C and contents allowed to react for 120 minutes. After the time set was achieved, the reactor headspace was discharged to vapour pressure of water value, assuming minimum temperature drop occurred during headspace discharging. The vapour pressure of water at 220 °C is approximately 2.3 MPa. Oxygen pressure at 1 MPa was then charged into the reactor and the contents allowed to react for 120 minutes.

Where presented, error data in this report was calculated at a 95% confidence interval and represented with error bars on the graphs.

## **2.4 PRODUCT ANALYSIS**

After the reactions, samples were collected and sent for analysis. The water quality parameters, ammonia, TSS, VSS, TCOD, and SCOD were measured following standard analytical procedures (APHA, 1989). The concentration of carboxylic acids was determined by an inhouse method involving pH correction, with formic acid followed by capillary gas chromatography with flame ionisation detection (GC-FID). The column used was a 30 m x 0.53 µm ID Nukol™ ramped from 30 °C to 150 °C. Butan-1-ol solution was used as the standard. The total residual organic carbon concentration (TOC) in filtered samples was also measured with a TOC analyser (Elementar High TOC II).

## **3 RESULTS AND DISCUSSION**

Total COD (TCOD) and soluble COD (SCOD) was analysed for the feed and process products. The results were normalised to a COD per unit feed solids (Fig.2 a). Particle COD (PCOD) is the difference between TCOD and SCOD.

The data in Fig. 2(a) clearly indicated that the initial soluble COD level of approximately 200 kg COD/t DS was more than doubled as a result of treatment under the different process conditions. Thermal hydrolysis conditions at low temperature and no oxidant achieved 50 % COD destruction and accumulated 60 % more soluble COD. Wet oxidation and two – stage processes achieved 70 % and 60 % COD destruction respectively which culminated into 50 % and 60 % soluble COD accumulation. The difference in destruction and accumulation was as a result of oxidation of the soluble COD under the various process conditions. The presence of oxidant, as in

wet oxidation and two – stage mainly converts the dissolved organic matter into non – organic end products. The greater accumulation of soluble COD in the thermal hydrolysis process reflects a lack of destruction of the hydrolysed material, compared with the oxidative processes. In effect, the two – stage process achieved more soluble COD with less COD destruction compared to the wet oxidation process. Fig. 2 (b) shows the product TOC achieved for each process. The trends are similar to the changes in soluble COD.

Analysis of carbohydrates was conducted as shown in Fig. 3. Thermal hydrolysis had the most significant proportion of carbohydrates detected, glucose as the most dominant carbohydrate produced. Low concentrations of glucose were achieved during the wet oxidation and the two – stage processes. As a result it ultimately showed that at higher temperature processes (wet oxidation and two – stage) the carbohydrates undergo cleavage into other forms of carbon bearing compounds. Jin et al.2005, postulated that when carbohydrates are subjected to aggressive thermal – wet oxidation conditions (300 °C), acetic acid can be produced through two competing reaction pathways. The pathways involve decomposition in the first stage either via furans or lactic acid formation prior to oxidative production of acetic acid.

Analysis of the VFAs was carried out on each of the process product liquors presented in Fig.4 as a yield normalised to dry biosolids feed into the reactor. The resulting profile shows that acetic acid was the dominant VFA fraction in all the processes. The highest concentration was achieved in the wet oxidation process followed by the two – stage process. Relatively low VFA concentrations were achieved in the thermal hydrolysis reaction. VFAs contributed significantly to the soluble COD achieved in the wet oxidation and two – stage processes. Acetic acid was found to be the dominant compound present in the process liquors with lower concentrations of formic acid also identified in the wet oxidation and two – stage processes. The highest yield of acetic acid was observed in the wet oxidation process, achieving about 146 kg/t dry solids feed. About 90 kg/t dry solids feed was achieved in the two – stage process.

Furthermore, when acetic acid is required for downstream separation/utilisation, both the yield and purity of acetic acid are important parameters. The acetic acid yield is defined as the percentage of the original sludge organics which is made up by the final acetic acid product, expressed on a carbon basis. The acetic acid purity is defined as the percentage of the residual soluble organics which is made up by the acetic acid product, again

expressed on a carbon basis (Jin et al., 2005). Fig. 5 shows that the acetic acid yield obtained by the thermal process increased from 0.37 % in the thermal hydrolysis process to 12.2 % during the single stage wet oxidation, with moderate yield of being observed at 7.6 % for the two – stage process. The purity of the acetic acid improved from about 1 % in thermal hydrolysis to about 37.6 % in the WO process. The two – stage process achieved acetic acid purity of about 23.9 %. The product distribution in the two stage process included a wider range of carbon bearing compounds hence lower acetic acid purity was achieved.

The relative distribution of VFAs and soluble carbohydrates to the soluble TOC is summarised in Fig.6. This clearly shows that the contribution of VFAs in the product liquor was very low within thermal hydrolysis and improved significantly to dominate the identified soluble carbon produced during wet oxidation.

The work demonstrates no enhancement of acetic acid production by the two-stage system described here. This is in contrast to the work of Jin et al., (2005), who describe an increase in acetic acid yields from 9-11% for a single stage oxidation (similar to our work), up to 16-20% for their two-stage process. Acetic acid purity was shown to rise from 26-33% (again similar to our work), up to 68-75% for their two-stage process. The initial hypothesis of this work is thus not supported, and at least one of the factors which differ between our work and those of Jin et al., (2005) - substrate specificity, reaction severity (temperature-time profile) or oxidant type – is clearly important in achieving the reaction mechanisms which support enhanced organic acid production. A mechanistic explanation for these differences is beyond the scope of the current results, and should be targeted in future work. We note that, at a minimum, the purity of acetic acid within the process liquors is likely to be enhanced by raising temperatures towards those used by Jin and co-workers (300 °C), due to acetic acid being one of the most recalcitrant organics to breakdown in sub-critical oxidation.

## **4 CONCLUSIONS**

This work has demonstrated that organic acids can be produced as products for potential beneficial re-use through targeting biosolids conversion (deconstruction) rather than destruction in hydrothermal systems. Significant concentrations of small organic molecules were produced in the wet oxidation and two – stage processes. Acetic acid was found to be the dominant compound present in the process liquors with lower

concentrations of formic acid also identified. Carbohydrates were found to be dominant in the thermal hydrolysis process.

Although hydrolysis facilitates the transformation of solid components into liquid phase, it was shown that combining the processes in stages with wet oxidation did not optimise the acetic acid generation as expected. Contrary to results obtained by other workers (Jin et al., 2005) in this field, which showed high yields and purity of acetic acid during the two – stage process compared to the wet oxidation process, we achieved higher acetic acid yield and purity during the single-stage wet oxidation process. A mechanistic understanding which can reconcile these results awaits future experimental and theoretical approaches.

Fig. 1: Schematic diagram of the wet oxidation reactor system. (1- Reactor, 2-Thermocouple, 3 - Cooling coil, 4-Stirrer, 5-Heater, 6-Controller, 7-Gas cooler, 8-Pressure regulator, 9 - Sampling system, 10- Oxygen cylinder)

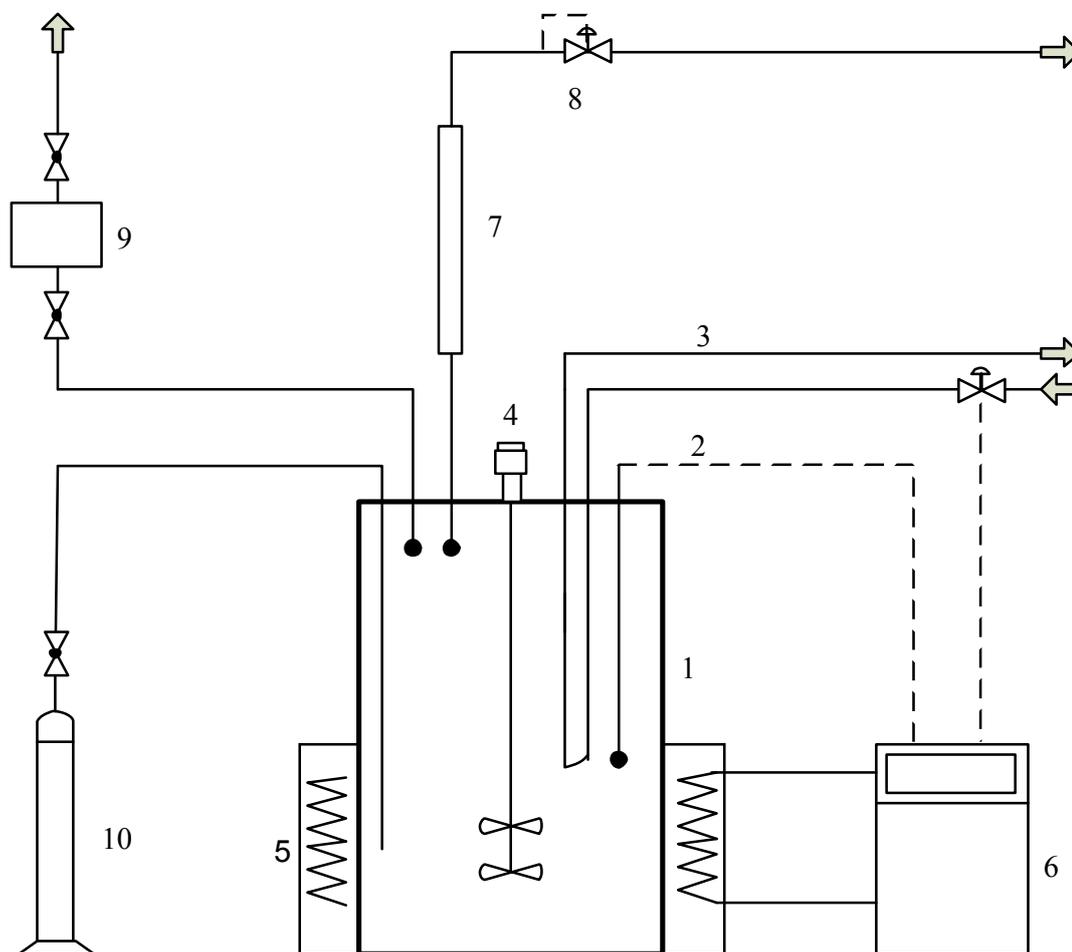
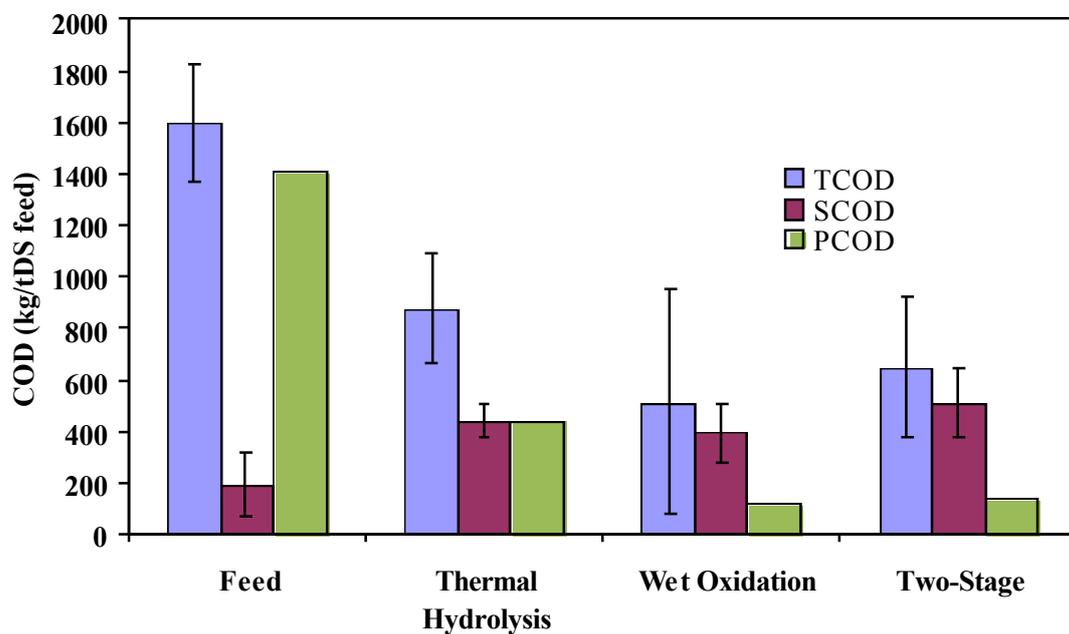


Fig. 2: Comparison of a) COD and b) soluble TOC concentrations achieved in the processes

(a)



(b)

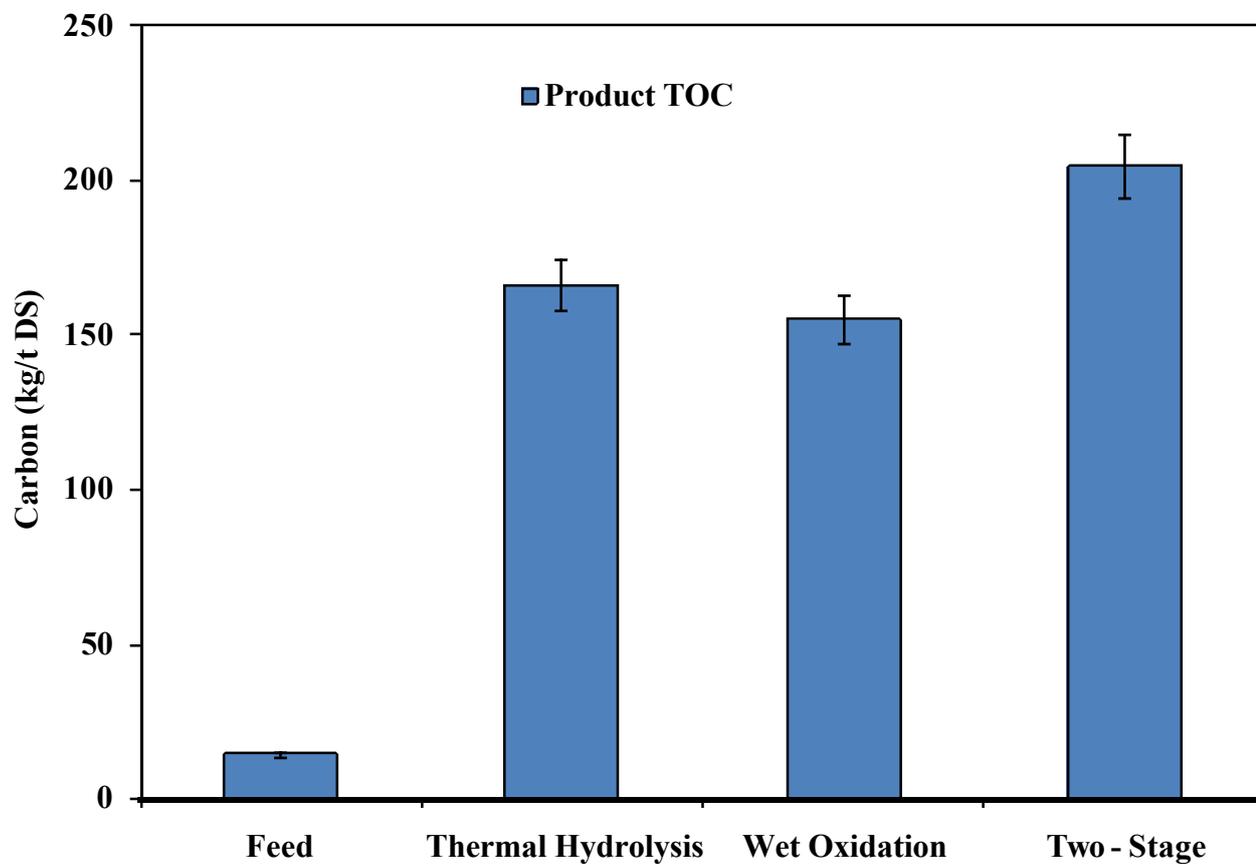


Fig. 3: Contribution of carbohydrates based on carbon

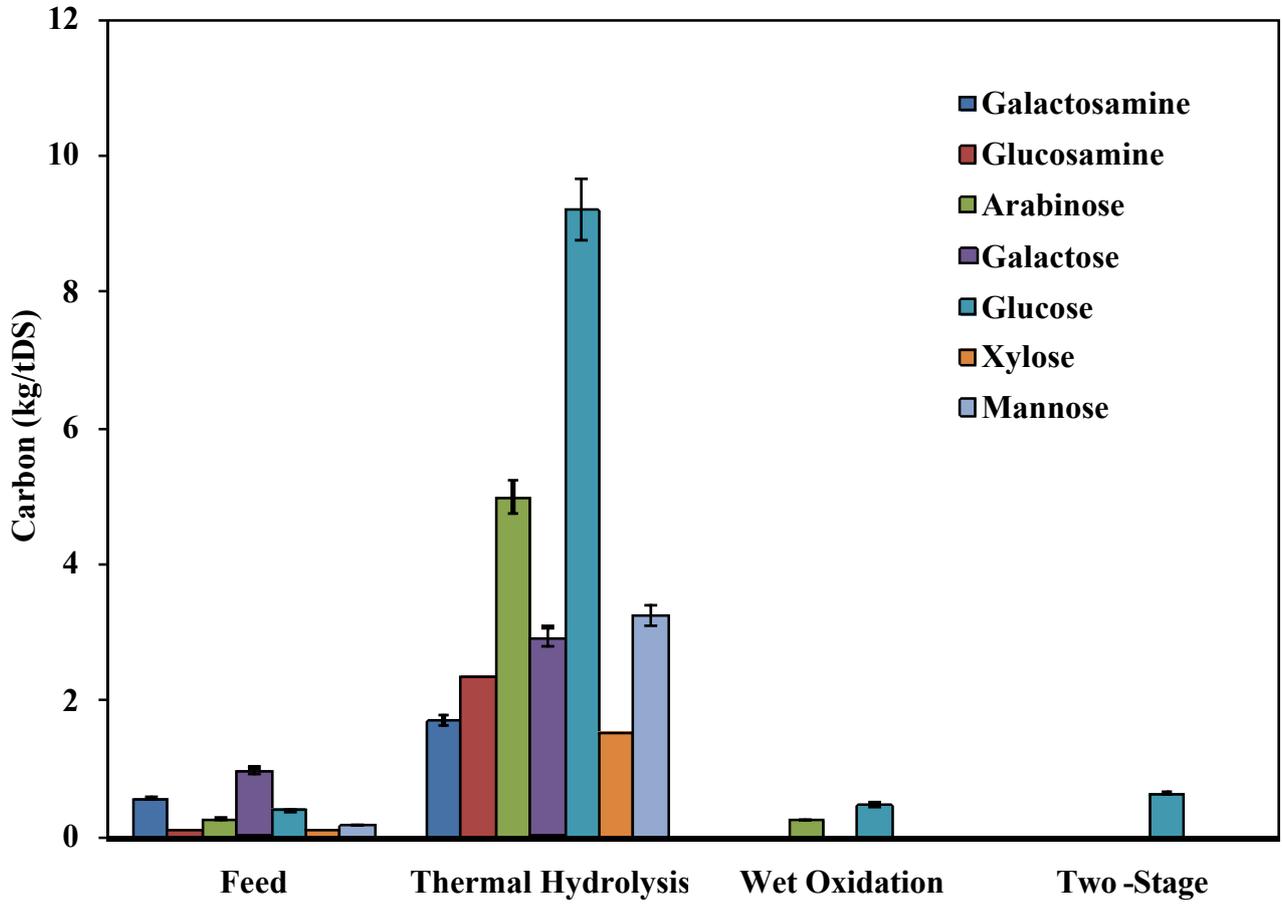


Fig. 4 Comparison of VFA compounds in the process liquors.

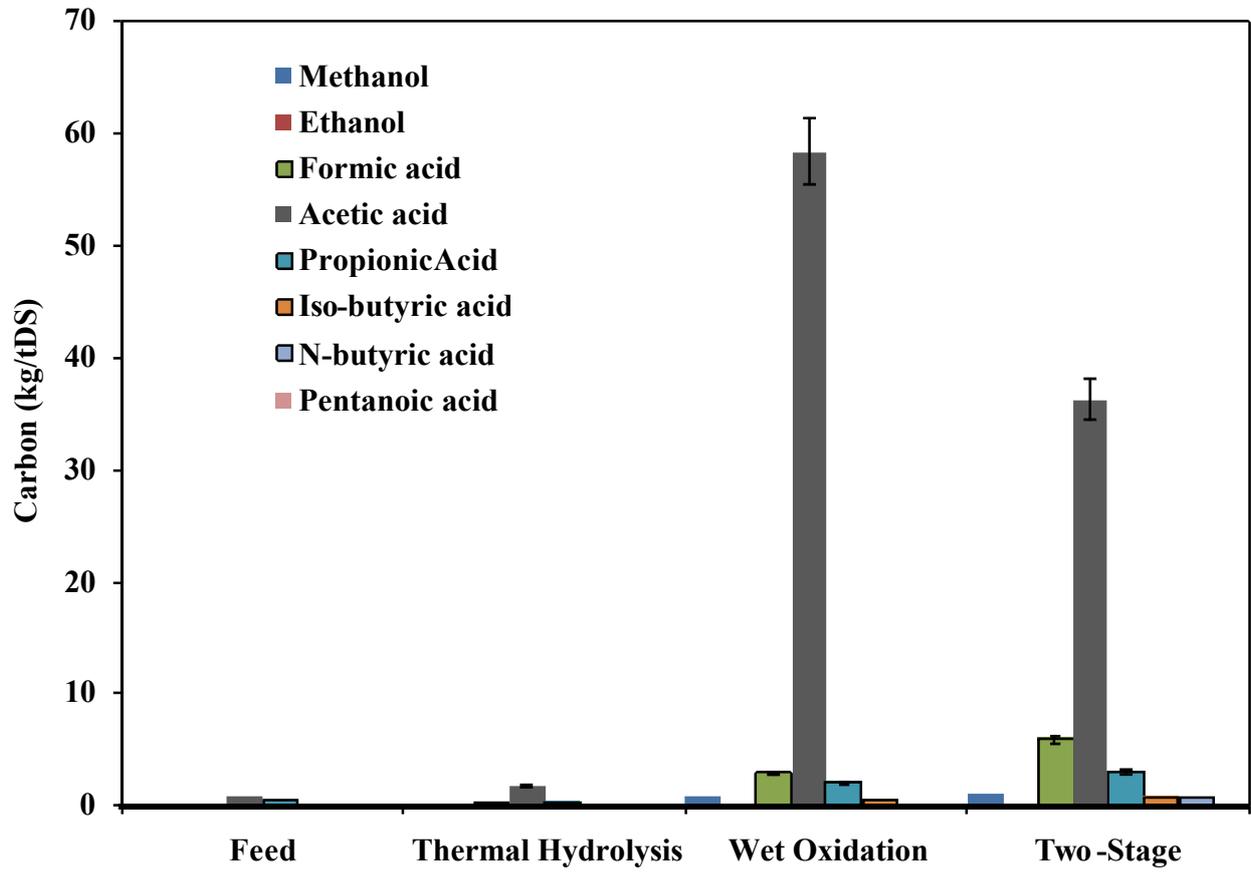


Fig. 5 Comparison of acetic acid yield and purity.

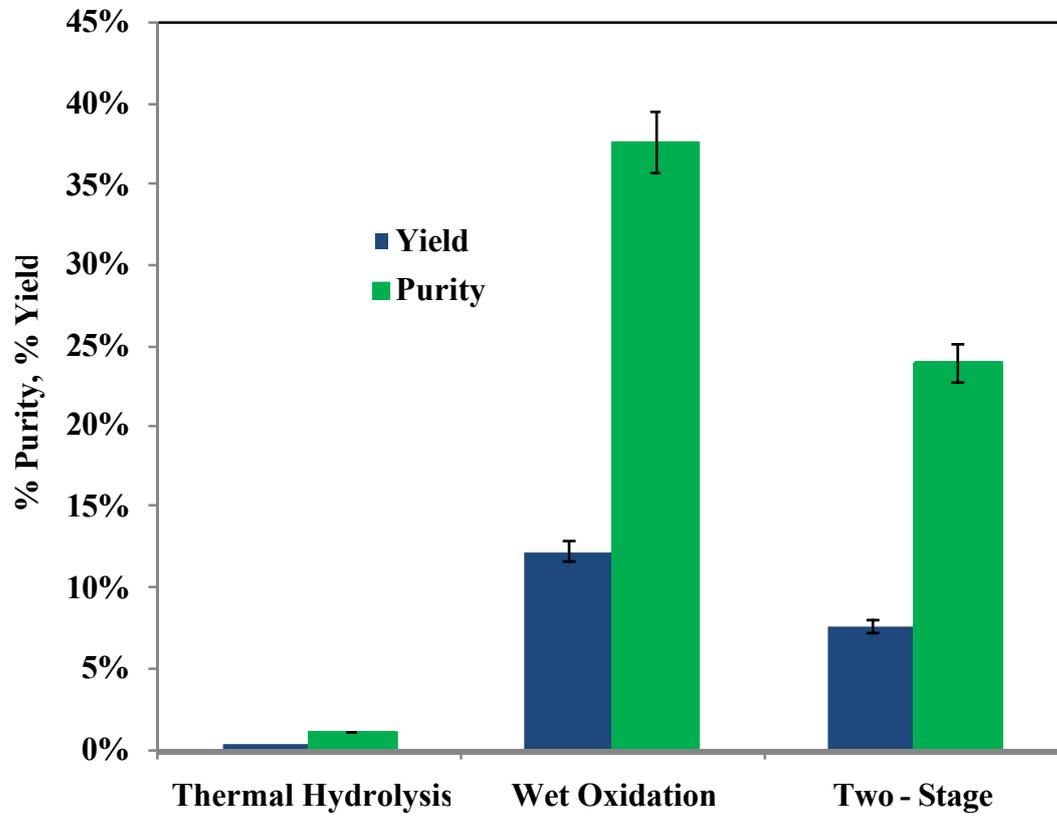
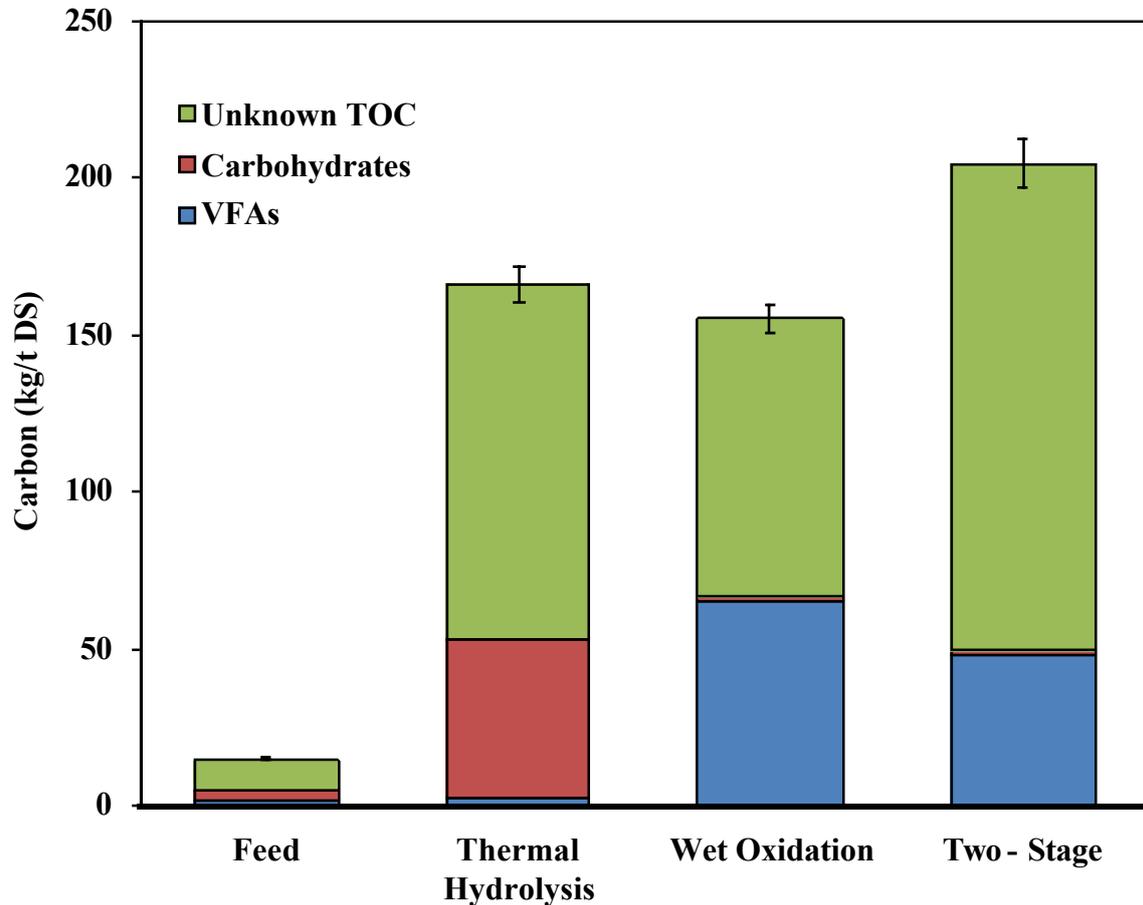


Fig. 6 Comparison of acetic acid yield and purity.



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