

# Catalytic hydrothermal gasification of biomass

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**Abstract:** A recent development in biomass gasification is the use of a pressurized water-processing environment to avoid drying of the biomass. This paper reviews the research undertaken developing this new option for biomass gasification. This review does not cover wet oxidation or near-atmospheric-pressure steam-gasification of biomass. Laboratory research on hydrothermal gasification of biomass focusing on the use of catalysts is reviewed here, and a companion review focuses on non-catalytic processing. Research includes liquid-phase, subcritical processing as well as supercritical water processing. The use of heterogeneous catalysts in such a system allows effective operation at lower temperatures, and the issues around the use of catalysts are presented. This review attempts to show the potential of this new processing concept by comparing the various options under development and the results of the research. © 2008 Society of Chemical Industry and John Wiley & Sons, Ltd

**Keywords:** hydrothermal gasification; biomass; biomass gasification

## Introduction

Gasification of biomass by thermal methods involving pyrolysis and/or partial oxidation is well-known as a method to produce a fuel gas or a synthesis gas, composed of carbon oxides and hydrogen. Typical methods use a dry biomass feedstock with typically <10 wt% moisture. Much of the biomass resource is composed of material with higher levels of moisture, more typically 50 wt% and some even consists of wet biomass or biomass in water slurries at 85 wt% moisture or higher. To efficiently process such a resource a different technology is required and gasification in a pressurized water environment (hydrothermal gasification) is a concept under development around the world.

Hydrothermal gasification can be practiced over a range of operating temperatures and pressures. Early work identified supercritical water as an important operating medium with the supercritical condition being the overriding parameter. Later work has shown that subcritical water can also be useful for highly effective gasification when performed with active catalysts. Figure 1 is a flow diagram of the basic system for continuous-flow catalytic hydrothermal gasification. It suggests the importance of heat recovery in efficient operation. The only input is the biomass/water slurry, and a simple separation of fuel gas and water follows the catalytic treatment. A useful update of the work in several laboratories using conditions on both sides of the critical point of water was recently published demonstrating the extent of interest in the concept.<sup>1</sup> The use of catalysts in hydrothermal gasification

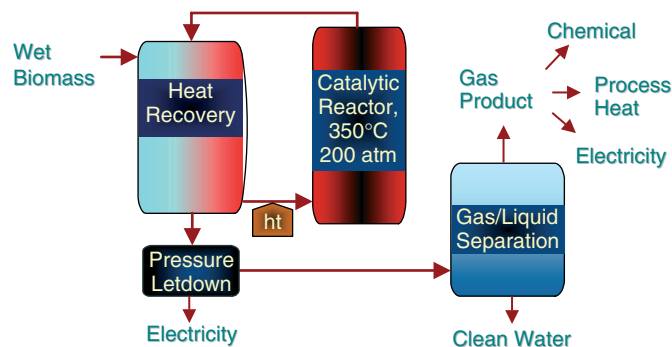


Figure 1. Catalytic hydrothermal gasification at subcritical conditions.

of biomass is the subject of this review. A companion review by Kruse<sup>2</sup> provides a review of hydrothermal gasification biomass without the use of heterogeneous metal catalysts.

The temperature used in the operation of hydrothermal gasification of biomass can have several significant effects. In the review by Osada *et al.*<sup>3</sup> three temperature regions for hydrothermal gasification are identified:

1. Region I (500–700 °C supercritical water) biomass decomposes and activated carbon catalyst is used to avoid char formation (described later in this review) or alkali catalyst facilitates the water-gas shift reaction (see Reference 2 for more discussion).
2. Region II (374–500 °C, supercritical water) biomass hydrolyzes and metal catalysts facilitate gasification.
3. Region III (below 374 °C, subcritical water) biomass hydrolysis is slow and catalysts are required for gas formation.

When operating in a system which reaches thermodynamic equilibrium, the resulting gas product composition will be determined by the pressure and temperature. Operation at subcritical temperature results in a product gas high in methane and less hydrogen<sup>4</sup> while operations at supercritical temperatures will produce more hydrogen and less methane. A confounding factor is that the partial pressure of water in the system will also affect the gas product composition in that lower biomass concentration in the reactor system – and therefore higher water content – will move the equilibrium toward hydrogen and away from methane by known steam-reforming mechanisms. A useful catalyst for gasification of biomass structures will also be a useful catalyst for methane synthesis and reforming. The use of a catalyst can allow low-temperature operation while maintaining useful kinetics. The use of low temperature will also impact the mechanical systems for containing the reaction. Lower temperature operation allows lower capital costs because of lower pressure operation, requiring less containment structure, and less severe attack on the reactor walls, which allows the use of less costly alloys.

### Early developments in catalytic hydrothermal gasification:

Model's papers are among the first to describe hydrothermal gasification. Those papers claim a dramatic effect above the critical point of water wherein no solid byproducts are produced. The results from batch tests with a range of catalysts (Table 1) show little effect of catalyst. Particularly

Table 1. Hydrothermal gasification of carbohydrates.

Feedstock	Catalyst	Temperature	Pressure	Time	Liquid	Gas	Solid	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> <sup>+</sup>
Glucose	None	200	13.6	2h	69.1	0.03	29.8	Not analyzed				
Glucose	Ni	200	13.6	2h	61.6	ND	ND	Not analyzed				
Glucose	Ni	250	40	2h	74.2	0.2	ND	Not analyzed				
Glucose	None	300	83	2h	33.9	0.3	39.0	Not analyzed				
Glucose	Ni	300	83	2h	47.3	0.3	28.3	Not analyzed				
Glucose	Ni	350	165	1h	ND	ND	11.0	Not analyzed				
Glucose	None	374	218	1h	77.8	8.2	—	25.8	1.3	34.4	38.5	—
Glucose	Ni	374	218	1h	86.8	10.0	—	30	1.5	42	27	—
Glucose	Mixed	374	218	0.5h	65.0	20.2	—	45.1	3.2	38.5	12.5	0.7
Glucose	Mixed	374	218	0.5h	70.8	23.2	—	43.1	2.9	40.6	12.6	0.8
Cellulose	Mixed	374	218	0.5h	77.47	18.31	—	14.5	1.5	19.7	64.2	0.1

After Modell<sup>6</sup>.

noteworthy is that there was very little methane synthesis accomplished, despite commentary claiming high-Btu gas production and the author's understanding that higher methane content was suggested by thermodynamic equilibrium calculations.<sup>5</sup> Below the critical point of water, at 350 °C, the gas yield was insignificant, with or without nickel catalyst. The nickel catalyst listed was commercially produced in an oxide form. It is apparent from the low methane yield and gasification result that the catalyst was not active. The mixed catalyst including nickel oxide formulations with alumina and platinum formulations also exhibited hardly any activity.

Subsequent work by Elliott *et al.* demonstrated that the use of active catalysts can facilitate the hydrothermal gasification of biomass, even below the critical point of water. Their initial work compared biomass hydrothermal gasification below and above the critical point of water and with and without catalysts.<sup>7</sup> Biomass feedstocks included cellulose, lignin, hollocellulose (cellulose and hemicellulose), and a Douglas fir wood flour. In batch tests using a nickel catalyst with and without added sodium carbonate co-catalyst, the effect of temperature from 350 to 450 °C was evaluated. Significant improvements when using the nickel metal catalyst were noted including higher gas yields and higher levels of methane in the product gas. In Table 2, results are presented showing much higher gasification and methane levels and reduced levels of carbon monoxide compared to that reported by Modell. The higher gasification is notable because it is accomplished with wood, a more complex and less reactive feedstock compared to glucose or cellulose. The authors reported no remarkable transformation in the system in passing the critical point of water, but only

the expected increased rate in gasification as a result of higher temperature. The Sealock and Elliott<sup>8</sup> patent further describes results with a number of biomass feedstocks, which can be gasified at these temperatures in the presence of a nickel metal or alkali-promoted nickel catalyst. The patent claims the formation of a fuel gas composed primarily of methane, carbon dioxide and hydrogen. They also report that cesium seems to be more active than potassium or sodium as measured by carbon conversion to gas (ranging from 79% down to 68%, with Cs > K > Na) and mass of CH<sub>4</sub> produced (ranging from 15.3 g per 100 g cellulose down to 11.5 g after 15 min at 400 °C).

An additional significant development underlying the development of catalytic hydrothermal gasification was the understanding of stable formulations of high-surface-area support materials for the catalysts that are useful in hot water systems. In order for catalysis to be an effective adduct for hydrothermal gasification, materials with long-term stability in hot liquid water needed to be identified and utilized in catalyst formulations. Elliott *et al.*<sup>9</sup> were the first to identify the problem and provide solutions. As shown in their research, a range of alumina- and silica-based materials, commonly used for catalyst formulations in the petroleum and gas processing industries, were less useful for hydrothermal gasification. By using a number of commercial catalysts in their research they found that silica, aluminas (other than  $\alpha$ -alumina), various ceramic supports, minerals, such as kieselguhr, and other silica-aluminas were unstable in a hot liquid water environment. Mechanisms such as dissolution, phase transition, and hydrolysis were identified. Of the many tested materials, the useful supports identified included carbon, mono-clinic zirconia or titania, and  $\alpha$ -alumina.

**Table 2. Catalytic hydrothermal gasification of wood flour.**

Feedstock	Catalyst	Temperature	Time	Gas, % of C fed	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> <sup>+</sup>
Wood flour	None	350	1h	15					
Wood flour	Ni/Na	350	1h	42	39	12	49	0	1
Wood flour	Ni/Na	370	1h	—	38	15	46	0	1
Wood flour	Ni/Na	380	1h	—	34	16	49	0	1
Wood flour	None	400	1h	19	—	—	—	—	—
Wood flour	Ni/Na	400	1h	67	35	24	41	0	1

After Elliott and Sealock<sup>7</sup>.

## Development of base metal catalysis for hydrothermal gasification

From the early results in hydrothermal gasification it was clear that a range of activities were evident with different catalysts. Although Modell's<sup>6</sup> mixed catalyst test involved base metals (nickel, cobalt and molybdenum as oxides) the low level of activity suggests that these metals might not be useful for catalytic hydrothermal gasification. Elliott *et al.*<sup>9</sup> did a more detailed assessment of other base metals to determine activity. Their study suggested that only nickel in a reduced form had any significant amount of activity. Copper on zinc oxide and a cobalt catalyst had slight activity as demonstrated by low levels of methane production. Other catalysts containing tungsten, molybdenum, zinc, or chromium showed no useful activity. Other tests<sup>10</sup> showed that other inactive base metals were rhenium, tin, and lead. A common result was the oxidation of the metal in the hydrothermal system. Nickel and copper were the only base metals found to remain reduced in the metallic form after the test. Nickel was found to be active in numerous formulations, but these had varying useful lifetimes depending on the support material. It is not surprising that nickel would be a noticeably more active catalyst, as it is well-recognized for its usefulness in steam-reforming of hydrocarbons and for methane synthesis from hydrogen and carbon monoxide.

Nickel catalysis of hydrothermal gasification has been investigated by a number of research groups over the past 15 years. The group of Elliott *et al.*<sup>9</sup> evaluated a number of commercial catalyst formulations before focusing on one product. Though a few useful catalysts were found, these inevitably had limited useful lifetimes (<100 h). The formulations in almost all cases showed signs of support breakdown and nickel crystallite sintering under hydrothermal conditions in either batch or continuous-flow tests. The tests included supports such as those mentioned earlier as well as the use of Raney nickel metal and nickel metal powder. The most useful formulation exhibited a limited sintering property, such that after an initial period of sintering lasting about 100 h, a stable crystallite remained for the balance of a 700-h continuous-flow test.

Minowa's group also evaluated several nickel catalyst formulations in hydrothermal gasification of glucose and cellulose. The initial work<sup>11,12</sup> was with a kieselguhr support

which was replaced in later studies by a silica-alumina support.<sup>13</sup> However, these were short batch tests (1 h) and none were performed for extended time. No assessment of catalyst lifetime was made. In addition, Minowa's group reports a comparison of several different silica and alumina supports and suggests that the catalysts give different levels of activity.<sup>14</sup> It is unclear from the data whether the support composition is the controlling factor and, again, no lifetime assessment is included.

The first report by Vogel's group was of the use of  $\alpha$ -alumina supported nickel in comparison to Raney nickel.<sup>15</sup> In small batch tests, high yields of methane were achieved and nearly tar-free byproduct water, i.e., nearly complete gasification of wood at temperatures from 370° to 420°C. The Raney nickel catalyst was clearly more active, and the  $\alpha$ -alumina supported catalyst was abandoned. Catalyst lifetime was recognized as a process necessity for economical operation although it was not assessed in these tests. In subsequent continuous-flow reactor tests Raney nickel was found to be deactivated over time in a 50-h experiment.<sup>16</sup>

The use of a nickel on an alumina-magnesia spinel formulation in a small continuous-flow reactor was reported by Pedersen.<sup>17</sup> The tests extended over a 100-h period and showed dramatic loss in methanation activity while maintaining significant gasification potential for phenol in water.

Stable nickel metal catalysts were developed by Elliott *et al.*<sup>10</sup> by impregnating promoting metals onto the most stable nickel catalyst formulation. These formulations were patented in 1998 and 1999.<sup>18,19</sup> The most useful promoter metals were copper, silver, and tin, impregnated at 1 wt%, while ruthenium was also useful and had the additional benefit of useful catalytic activity, as will be discussed below. These stabilized catalysts had useful activity (99.0% COD reduction @ 1.7 LHSV) at demonstrated lifetimes of >6 months in a laboratory test processing 10 wt% phenol in water at 350°C. This stabilization method was attempted with Raney nickel by Vogel *et al.*<sup>20</sup> and although stability was improved over their earlier results with plain Raney nickel, deactivation was still evident over 100 h of intermittent operation over three months processing a synthetic liquefied wood mixture of model compounds.

Another stable nickel catalyst has been reported by Miura's group.<sup>21</sup> This special formulation involved a carbon support,

which was formed by ion-exchanging nickel onto a resin and then carbonizing the resin. The resulting catalyst had a high nickel content (47%), dispersed on a high-surface-area carbon 170 m<sup>2</sup>/g which was relatively dense, 1.21 g/cm<sup>3</sup>. The high loading potential of this catalyst allowed effective conversion at high processing rates. Nearly stable activity was demonstrated over a 50-h continuous-flow test processing 0.2% phenol in water, but some sintering of the nickel was evident.<sup>22</sup>

### Development of noble metal catalysis for hydrothermal gasification

Although Modell's mixed catalyst system<sup>5,6</sup> included a noble metal, platinum, there was no indication of its utility as a catalyst for hydrothermal gasification. Tests with phenolic model compounds by Elliott *et al.*<sup>9</sup> showed that platinum and palladium had very low activity for hydrothermal gasification at 350 °C while ruthenium and rhodium had useful levels of activity. Later results showed even iridium had activity, but not silver.<sup>10</sup> Ruthenium showed long-term stability when used in gasification of phenol as a model compound. Particularly useful was the use of the rutile form of titania as the support, with a demonstrated activity for over 3000 h. The carbon-supported form showed an even higher level of activity. A recent test has demonstrated this catalyst with over 2000 h of stable activity processing a chemical manufacturing wastewater with over 10 wt% organic.

Subsequent work has been undertaken in several laboratories. Osada's group reported gasification of alkyl-phenols with several noble metal catalysts at 400 °C.<sup>23</sup> Their results confirmed that ruthenium and rhodium were the most active with notable gas production with high levels of methane after only 15 m at temperature, while platinum and palladium produced almost no gas with lower levels of methane and higher levels of hydrogen. They also studied the stability of three ruthenium catalysts<sup>24</sup> at 400 °C using lignin as the feedstock and found the titania (anatase)-supported catalyst to be stable. The carbon supported catalyst showed slight evidence of metal crystal growth with resulting loss of activity. An alumina-supported catalyst was destroyed in the process as the alumina changed phase from  $\gamma$ - to  $\alpha$ - and ruthenium was dissolved into the water.

Vogel's group has compared ruthenium catalysis with nickel using the synthetic liquefied wood mixture as the feedstock.<sup>25</sup> The skeletal nickel metal catalyst was found to sinter rapidly at 400 °C, even when stabilized by ruthenium doping, while a Ru on carbon catalyst was stable during 220 h of testing. In addition, tests with added sulfate (4 to 16 ppm sodium sulfate) showed that catalyst poisoning occurred even at low concentrations. Formation of a stable Ru III sulfate complex was proposed as the deactivating mechanism.

Other, seemingly contrary, results have been reported at both higher and lower temperatures using simple sugars or alcohols as feedstock at low concentrations. Cortright *et al.* have reported that platinum is a useful catalyst at low temperature (225–265 °C) for hydrogen production (with minimal methane) from simple oxygenates, including glucose, glycerol or methanol at a low concentration of 1 wt%.<sup>26</sup> Further results claim that the activity for several metals for ethylene glycol gasification (on a carbon dioxide production basis adjusted for CO chemisorption measurements) at 210 °C as: Pt ~ Ni > Ru > Rh ~ Pd > Ir.<sup>27</sup> However, on a total carbon gasification basis adjusted for amount of catalytic metal, the hierarchy is somewhat different: Ru >> Pt > Rh ~ Ni > Pd. The level of conversion in these experiments at 210–225 °C, with a higher concentration of ethylene glycol (10 wt%) is quite low, but the space velocity is not specified. Byrd *et al.* have reported that at 700 °C ruthenium on alumina catalyzes glucose (<5 wt%) gasification to hydrogen with a lower level of methane than in the absence of catalyst.<sup>28</sup> Meanwhile, Potic reports that a ruthenium on titania catalyst is useful for glucose (10 wt%) gasification at 600 °C and promotes methane formation with conversion of carbon monoxide and higher hydrocarbons.<sup>29</sup>

### Development of activated carbon catalysis for hydrothermal gasification:

Antal's group has identified activated carbon as a catalyst for hydrothermal gasification at supercritical water (600 °C) conditions. Xu *et al.* described the use of several charcoals as catalysts for gasification of biomass and chemical wastewater feedstocks.<sup>30</sup> With 1.2M glucose, a 34 s residence time (22.2 WHSV) results in 80% carbon gasification without catalyst and 103% gasification with the carbon catalyst. At



a 16 WHSV, the carbon gasification efficiency at 600°C was independent of operating pressure with 99% achieved at either 34.5 MPa or 25.5 MPa. However, the gasification drops from 98% at 600°C to only 51% at 500°C with a 1.0M glucose feedstock processed at 13.5 WHSV. Deactivation of the carbon catalyst toward gasification was observed after less than 4 h of operation. Operation with a swirl at the entrance allowed operation at near 100% for up to 6 h.

Tests with more complex biomass streams showed reduced rates of reaction.<sup>31</sup> Higher temperatures (650 to 715°C) were used to achieve high conversions (91 to 106%) with corn starch and sawdust in corn starch slurries. In these experiments, flow of feed was eventually halted by buildup of coke and ash in the heatup zone of the reactor. Metals present in the Hastelloy reactor wall appeared to catalyze the reactions. Such nickel alloy tubes are not suitable long-term for use at these processing conditions. Metals from the reactor wall were found in the activated carbon catalyst.

More recent work reported by Matsumura's group shows results with a suspended activated carbon catalyst with a pretreated chicken manure feedstock.<sup>32</sup> In this processing mode, the plugging in the reactor was avoided for up to 4 h of operation at 600°C and 25 MPa. Recovery and reuse of the catalyst is perceived as a simple process step.

## Biomass gasification results with nickel catalysis

Gasification of biomass has been demonstrated in a hydrothermal environment with active catalysts over a range of temperatures, both above and below the critical point of water. Actual biomass feedstocks have been processed as water slurries over a heterogeneous catalyst in both batch and continuous-flow reactor systems. Early results in a batch reactor showed that a wide variety of high-moisture (~10 wt% dry solids) biomass feedstocks could be converted to a gas product containing a high level of methane.<sup>4</sup> The data in Table 3 show high conversion at 15 m at 400°C and the important yield of methane in the presence of a nickel metal catalyst. But these results, using an alumino-silica-supported nickel catalyst, demonstrate only short-term catalyst activity. A special note is that the addition of alkali to the processing system (in conjunction with less nickel catalyst) resulted in a reduced methane product and increased hydrogen product.

Related batch test results also showed the production of methane as a secondary gas product over the time at temperature at the expense of hydrogen and carbon dioxide. From these results was concluded that the biomass composition, particularly the non-carbohydrate portion, played an important role in the level of gasification achieved.

**Table 3. Catalytic hydrothermal gasification of wet biomass.**

Feedstock	Gas, % of carbon fed	CH <sub>4</sub> scf/lb	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> <sup>+</sup>
Cellulose*	97.6	5.5	3.9	43.2	47.8	0	3.7
Sorghum	94.6	5.5	9.5	38.4	50.5	0	1.6
Sunflower	87.8	5.1	5.0	45.7	45.5	0	2.4
Napier grass	100.8	5.2	6.9	40.6	51.1	0	1.4
Corn stover‡	72.9	1.5	20.1	16.3	62.0	0	1.3
Water hyacinth	73.1	4.0	11.3	35.9	49.6	0.8	0.9
Kelp	78.8	2.9	7.1	41.9	48.4	0	1.5
Douglas fir‡	49.8	2.6	21.6	29.0	47.6	0	1.8
Grape pomace	44.5	3.1	9.6	40.2	47.7	0	1.0
Spent grain	55.7	3.9	9.6	43.1	44.2	0	1.4
Potato waste‡	46.4	2.0	27.6	20.4	50.2	0	1.8

After Sealock *et al.*<sup>34</sup>

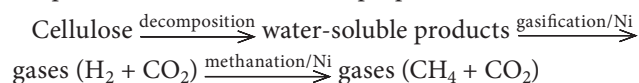
\*380°C.

‡sodium carbonate co-catalyst with lower (1/10) nickel loading.

This result was further studied with mixtures of actual lignins and cellulose by Matsumura's group with the same conclusion.<sup>33</sup> In the same study, deposition of tarry intermediates on the catalyst was also identified as a catalyst deactivation mechanism.

Results at lower temperature (350 °C) with a more active (and more stable),  $\gamma$ -alumina-supported nickel catalyst confirmed the catalytic hydrothermal gasification of some food processing waste biomass slurries as shown in Table 4.

The mechanism for cellulose gasification was also studied at this lower temperature by Minowa and Ogi<sup>14</sup> and a simplified reaction scheme was proposed:



In the same study, a collection of alumina and silica-alumina catalyst supports were evaluated and found to have varying activities, but the variation in activity was attributed not only to the kind of support but also to the catalyst particle size (not the surface area), indicating that only metal particles on the external surface could contribute.

Minowa's group<sup>13</sup> provided further elucidation to the reaction scheme given above in a related article. Cellulose decomposition through hydrolysis to water-soluble products was studied with and without alkali added to the reaction mixture. Decomposition of the cellulose to aqueous products, glucose, gases, tars, and char, at temperatures even below the 350 °C reaction temperature, was quantified. A role of alkali to stabilize oil formation by inhibiting char formation was identified. Study of reaction conditions down to 200 °C provided further insight into the reaction mechanism and elucidated

the role of the nickel catalyst for gasification of hydrothermally generated intermediates and methane synthesis.<sup>36</sup>

Vogel's group also studied nickel catalyzed hydrothermal gasification above and below the critical point of water.<sup>15</sup> Using wood as the feedstock at 10 to 30 wt%, high conversion of the biomass was achieved resulting in low-residual organic material in the water product (as low as 200 ppm organic carbon). Another important conclusion of this study was the finding of much higher activity using Raney nickel versus an  $\alpha$ -alumina supported nickel. Based on their calculations using thermodynamic equilibrium gas compositions, a 70% thermal efficiency could be achieved. Later studies confirmed these early results wherein Raney catalysis at 400 °C for 90 m resulted in a methane yield of 0.33 g/g of wood and the product gas contained 49% methane by volume.<sup>16</sup> XPS analysis of the nickel catalyst before and after use suggested a minimal amount of carbon deposition at the same time that the amount of reduced nickel was increased and the oxide decreased, suggesting little deactivation of the catalyst. Vogel also reported wood gasification tests with several doped skeletal nickel catalysts.<sup>25</sup> High gasification efficiencies were reported without doping or with Ru and high and low levels of Cu, but a Mo-doped catalyst had a lower activity than the nickel alone.

## Biomass gasification results with ruthenium catalysis

Elliott compared biomass gasification in a stirred batch reactor using both stabilized nickel and ruthenium catalysts.<sup>37</sup> As shown in Fig. 2 (also found in Reference 1) the most

**Table 4. Catalytic hydrothermal gasification of waste biomass slurries.**

Feedstock	% of COD conversion	Residual COD, ppm	H <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	CO	C <sub>2</sub> <sup>+</sup>
Corn DAF	84.6	18 750	11.0	35.7	50.4	0	2.4
Apple pomace	97.1	5 800	6.4	40.3	51.4	0	1.8
Apple seed peel	98.4	4 100	5.4	35.9	57.0	0	1.7
Potato crumbs	99.8	290	6.2	54.2	38.7	0	0.8
Potato flesh	99.7	475	7.0	45.9	45.4	0	1.4
Potato peels	99.2	680	10.0	43.1	45.1	0	1.8
Yellow onion	99.7	650	15.0	34.2	48.9	0	1.8
After Elliott and Hart <sup>35</sup> .							

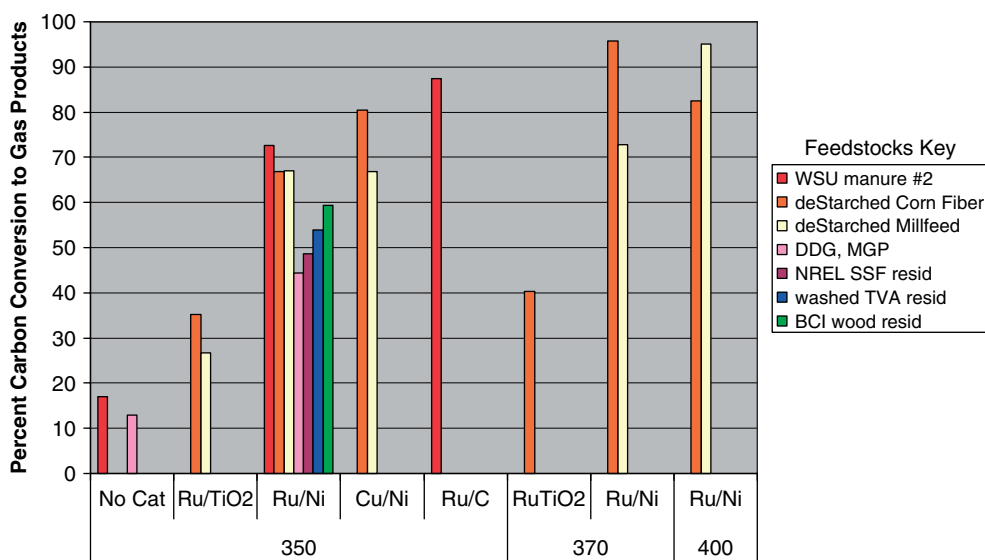


Figure 2. Batch reactor gasification of several biomass feedstocks.

active catalyst was a ruthenium on carbon support. The No Cat data show the limited conversion of biomass (dairy manure or distillers' dried grains) in the absence of catalyst. The RuTiO<sub>2</sub> was a 3 wt% Ru on a rutile form of titania shown to be a stable catalyst form for hydrothermal gasification. The Ru/Ni and Cu/Ni were stabilized nickel catalysts presented for comparison. The destarched products were generated from food-processing residues from corn wet milling and wheat dry milling. The NREL SSF, TVA, and BCI samples were hydrolyzed biomass fermentation residues. The results were after 4 h at the temperature given at the bottom of Fig. 2 (in degrees Celsius).

Osada *et al.* have also investigated a range of catalysts and biomass feedstocks in a small batch reactor.<sup>38</sup> After 15 m at 400 °C (37.1 MPa) the carbon gas yields from lignin range from 3.7% without catalyst to 5.5% with a nickel on alumina catalyst to 31.1% with a ruthenium on titania catalyst. For cellulose the same pattern emerged, 11.3% w/o catalyst, 17.3% with Ni, and 74.4% with Ru. The titania support was not specified, but its surface area was listed at 24.9 m<sup>2</sup>/g, suggesting that it was a mixture of anatase (unstable, high-surface area) and rutile (stable, low-surface area). Subsequent work compared a range of catalysts for lignin gasification with results as given in Table 5.<sup>39</sup> At this supercritical condition it was also found that

**Table 5. Lignin gasification results with several catalysts.**

Catalyst	Metal wt%	Amount of catalyst, g	Yield, %C as gas	TON*
Ru/TiO <sub>2</sub>	2	0.375	39.0	108
Ru/Al <sub>2</sub> O <sub>3</sub>	5	0.150	43.4	89
Ru/C	5	0.150	46.9	69
Rh/C	5	0.161	31.4	45
Pt/C	5	0.288	29.1	68
Pt/ Al <sub>2</sub> O <sub>3</sub>	2	0.720	20.6	47
Pd/C	5	0.158	13.9	33
Pd/ Al <sub>2</sub> O <sub>3</sub>	5	0.158	6.0	21
Ni/ Al <sub>2</sub> O <sub>3</sub>	17	0.300	4.8	6

\*TON = (mol of product gas carbon)/(mol of surface metal atoms, based on CO adsorption).

After Osada *et al.*<sup>39</sup>



the rate of gasification was dependent on the water density, increasing over the range of 0.1 to 0.5 g/cm<sup>3</sup>.

More detailed studies related to the effect of sulfur on ruthenium catalysts were reported by Osada *et al.*<sup>40</sup> For all the catalysts listed in Table 5, the addition of elemental sulfur to the reaction medium caused a drop in the turnover frequency to one-tenth of the level listed here. In addition, the form of the sulfur made little difference as the results with a Ru/C catalyst with sulfuric acid, thiophene, 4-hydroxythiophenol, 4-methylthiophenol, or 2-methyl-1-propanethiol were similar. In the presence of sulfur, the Ru/C catalyst acquired sulfur in both the S<sup>2-</sup> and the SO<sub>4</sub><sup>2-</sup> forms, whose combinations with the Ru were confirmed. In a related study ruthenium on titania catalyst was treated by soaking in aqueous sulfuric acid and dried.<sup>41</sup> This highly sulfur-treated catalyst contained 3.7 moles of S per surface mole of Ru and resulted in a carbon gas yield of only 21.0% after 3 h compared to 97.7% for the fresh catalyst. Model chemical tests showed that 4-propylphenol gasification was essentially stopped (carbon gasification reduced from 97.9% to 2.2%) by the sulfur treatment, suggesting poisoning of the carbon-carbon bond scission and methanation reaction sites, while formaldehyde decomposition and water-gas shift activity were unaffected. Finally, regeneration of the sulfur-poisoned catalysts was attempted.<sup>42</sup> Subcritical water treatment (250–300 °C, 3–10 h) improved the catalytic activity and sulfur analyses suggested that about three-quarters of the S was removed. Supercritical water treatment was less effective as the sulfur species were more soluble at lower temperatures. The addition of hydrogen peroxide was not useful for the regeneration.

### Continuous-flow catalytic gasification of biomass

The only reports of continuous-flow reactor tests of actual biomass slurries using a heterogeneous metal catalyst have come from the Pacific Northwest National Laboratory in the USA. Early continuous-flow experiments of hydrothermal gasification of biomass utilized nickel catalysts in a Carberry-type stirred tank reactor.<sup>43</sup> The results confirmed the earlier batch test results in that high conversion of biomass solids to gas were achieved with high concentrations of methane in the product gas using a number of

biomass feedstocks, such as sorghum, spent grain and cheese whey. Also seen in these tests was the rapid deactivation of the nickel catalysts used. Decomposition of the nickel catalyst and poisoning by mineral content in the feedstocks were suspected deactivation mechanisms.

Subsequent work was performed in a tubular reactor with a fixed bed of catalyst.<sup>44</sup> In the test, brewer's spent grain biomass (28 500–41 000 ppm COD) was processed. A more stable nickel catalyst was used and was effective (97.7% COD reduction @ 2.3 LHSV) over a few hours of operation but lost activity (71.2% COD reduction @ 2.0 LHSV) after that. Analysis of the used catalyst showed deposits of biomass derived minerals on the catalyst such as hydroxylapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH) and nickel subsulfide (Ni<sub>3</sub>S<sub>2</sub>). In a related test, a stirred tank preheater was used upstream of the tubular catalytic reactor. In this test, using a more concentrated stream of spent grain (61 500–65 000 ppm COD), a less definitive deactivation (initially 96.2% @ 1.3 LHSV reduced to 82.2% @ 1.7 LHSV) was noted. Following the test, in addition to catalyst coating, there was also a deposit in the preheater composed of hydroxylapatite and nickel subsulfide, but also iron phosphate, ammonium iron sulfate, potassium aluminosilicate, calcium carbonate, calcium magnesium sulfate, and anorthoclase, an alkali silicoaluminate. All of these precipitates were attributed to components in the biomass feedstock. In a follow-up test, the spent grain was acid-washed, filtered, and ion-exchanged to remove multi-valent cations, such as calcium and magnesium, before processing in the catalytic system.<sup>45</sup> Much higher conversion was achieved with this feedstock (98.3% COD reduction @ 3.5 LHSV).

In later tests in the tubular reactor only configuration, biomass slurry pumping difficulties became evident.<sup>35</sup> Processing of slurries of ground potato or apple peels were short-lived because of pump failures and plugging of solids at the front end of the catalytic bed. The plugging appeared to be primarily organic solids produced from partially pyrolyzed biomass. These short-lived tests verified the high activity (95.4% COD reduction @ 2.67 LHSV) of the ruthenium stabilized nickel catalyst for biomass gasification.

With the use of a stirred tank preheater, the initial pyrolysis of biomass solids was achieved and effective gasification could be demonstrated at the bench-scale and in a scaled-up

engineering demonstration unit.<sup>46</sup> Use of ruthenium catalyst allowed high conversion rates which were relatively stable over time. Processing dairy manure solids (99.78% COD conversion @ 2.09 LHSV) appeared stable over 14.5 h. A continuation of the test with distillers' dried grains and solubles led to slight catalyst deactivation (99.52% COD reduction @ 1.73 LHSV down to 95.48% @ 1.40 LHSV) by the end of another 14.5 h. A third test also reported using DDG&S ended with plugging in the front end of the catalyst bed caused by mineral precipitates (magnesium phosphate was a major component), as opposed to organic solids.

In the scaled-up reactor, the use of either a stirred tank preheater or a tube-in-tube heat exchanger was sufficient to liquefy the biomass solids prior to entering the catalyst bed. However, mineral precipitates from the biomass remained a significant problem leading to plugging at the front end of the catalyst bed. Deposits composed of magnesium, phosphorus and calcium were observed. An additional catalyst deactivation problem was also clearly identified by x-ray photometric spectrometry analysis showing sulfur highly associated with the ruthenium in the catalyst. Pumping of biomass slurries remained inconsistent using reciprocating pumps with ball check valves.

The problem of mineral deposits when processing biomass has recently been addressed. Elliott *et al.* have shown that mineral capture during the preheating stage can be accomplished using two representative biorefinery residues (corn ethanol stillage and destarched wheat millfeed).<sup>47</sup> In a bench-scale continuous-flow reactor system, 99.9% reduction of COD was achieved at a 1.5 LHSV. 0.8 to 0.84 liter of gas per gram of dry solids was produced consisting of 56–57% methane, 41–42% carbon dioxide, and 2% hydrogen. The mineral recovery system separated a sludge containing 80 to 91% ash which accounted for a carbon loss of 1–2%. Phosphate in the feedstock amounting to 940–2700 ppm was not detectable in the product water. No phosphorus deposit was found in the catalyst bed, and scattered particles of calcium, magnesium and silicon did not appear to have caused any significant amount of deposits or catalyst coverage.

Related work on gasification of biomass pyrolysis condensates was reported by Roy *et al.*<sup>48</sup> Nickel catalysts were used at 400 °C to effectively convert (95–96%) the high COD aqueous streams collected from vacuum pyrolysis. Deactivation by an

undetermined mechanism was noted as conversion dropped to 85% after 6 h on stream and continued down to a lower level in the subsequent 2 h of operation.

## Process economics

Vogel and Waldner have generated some process economic estimates for a supercritical application of the technology.<sup>49</sup> They conclude that using a wood feedstock \$67/tonne would yield a gas product valued at \$10.3/GJ (\$9.8/million Btu). The 182 wet tonne/day plant (39 467 l/h), operating at 420 °C and 30 MPA, would have an installed capital cost of \$5.9 million.

Ro *et al.* completed a system analysis for use of subcritical gasification with hog manure feedstock.<sup>50</sup> The analysis suggests that catalytic hydrothermal gasification of flushed swine manure feedstocks with solids concentration greater than 0.8 wt% can be a net energy producer. The installed capital cost for the 1580 l/h unit (serving 4400 head swine feeder-to-finishing farm), operating at 350 °C and 22 MPa, would be \$0.99 million. The net product gas would have a value of \$47 006 per year at \$8/million Btu. The authors conclude that the costs are higher than a conventional anaerobic digestion lagoon system; however, the high rate of conversion of the organic matter into gas drastically decreases the land requirement for manure application and resulting costs in transportation and tipping fees. In addition, the catalytic gasification process would destroy pathogens and bioactive organic compounds, it would produce relatively clean water for reuse, and the ammonia and phosphate byproducts have potential value in the fertilizer market.

## Summary

Catalytic hydrothermal gasification of biomass has been under development for over 25 years. Recognition of this processing concept and extension of its development outside the USA has only occurred in the last 12 years. The development has included recognition of the shortcomings of conventional catalyst formulations and advances in new catalyst formulations, including both supports and metals for use in hot water environments. Although the continuous-flow processing of biomass slurries with these catalyst systems has now been demonstrated with high conversion to gas and important yields of methane, commercialization still remains in the

future. Utilization of wet biomass waste streams in this technology holds great potential.

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