

Effects of Trace Contaminants on Catalytic Processing of Biomass-Derived Feedstocks

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Summary

Model compound testing was conducted in batch a reactor to evaluate the effects of trace contaminant components on catalytic hydrogenation of sugars. Trace components are potential catalyst poisons when processing biomass feedstocks to value-added chemical products. Trace components include inorganic elements such as alkali metals and alkaline earths, phosphorus, sulfur, aluminum, silicon, chloride, or transition metals. Protein components in biomass feedstocks can lead to formation of peptide fractions (from hydrolysis) or ammonium ions (from more severe breakdown), both of which might interfere with catalysis. The batch reactor tests were performed in a 300-mL stirred autoclave, with multiple liquid samples withdrawn over the period of the experiment. Evaluation of these test results suggests that most of the catalyst inhibition is related to nitrogen-containing components.

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Key Words: catalysts, trace minerals, protein, catalytic hydrogenation, hydrolysates

Introduction

In the USA, which is growing ever more dependent on imported oil, the use of biomass as a feedstock for chemical production provides an important opportunity for displacing petroleum and reducing this dependence. Converting biomass to value-added chemical products involves heterogeneous catalytic processing in aqueous phase, a relatively less studied area of chemical processing. Aqueous phase processing requires specific catalyst formulations that are different from those typically used in more common petrochemical processing involving non-aqueous or gas phase reaction environments (1,2). However, certain trace components in the biomass feedstocks, i.e., non-carbon, -hydrogen, or -oxygen components, are potential catalyst poisons, and their impact on the catalysts in aqueous phase processing must be considered. This paper discusses the results of extensive model compound tests conducted to evaluate the effect of trace contaminants on biomass processing rates and mechanisms.

Biomass is often referred to as a “clean” feedstock, most accurately pertaining to wood, which is low in mineral content; contains almost no sulfur or nitrogen; and is composed primarily of carbon, hydrogen and oxygen. However, other potential biomass feedstocks are more problematic. Bark has more mineral, sulfur and nitrogen and leaves and twigs (juvenile wood) even more so. Herbaceous biomass has significant levels of mineral content, as much as 10 to 15 wt%, and a relatively high nitrogen (2 to 4%) content as well as sulfur. Aquatic biomasses, such as kelp or algae, have particularly high mineral contents, especially the marine species. Finally, waste biomass often can contain higher levels of minerals (concentrated in the residue after degradation of the organic portions) and be further contaminated with soil.

When considering biomass as a source of chemical feedstock, it is also important to remember that it is not a homogeneous organic structure. The carbohydrate structures of terrestrial plants are composed of both 5-carbon and 6-carbon sugar polymers. The lignin component, which binds the polymers together, is an aromatic polymer of nominally propylmethoxyphenols. In addition, there are proteins and fatty acids/oils, as well as the trace biocomponents that incorporate much of the mineral content. Therefore, processing biomass to chemical products must take into consideration both its bulk chemical structure and its components.

In our program of process development for bio-based chemical products, we conducted extensive model compound testing to evaluate the effect of various biomass contaminants on catalytic processing. Specifically, we evaluated catalytic hydrogenation of sugars to sugar alcohols in the aqueous phase, using a supported ruthenium metal catalyst. The experiments involve reagent glucose and/or xylose sugar as the model of the biomass-derived hydrolysates. To the sugar solutions, we added various chemicals to model the contaminants, which are derived from biomass feedstocks in actual process applications. The tests involved small batch reactor experiments to determine changes in the rate of reaction and mechanistic modifications caused by various contaminants. Some of these tests were undertaken as part of a project to evaluate the recovery of glucose derived from wheat millfeed starch hydrolysis. Other tests were part of a project that addressed recovery and purification of sugars derived from dairy manure solids hydrolysis.

Methods

These experiments were designed to model the hydrogenation process being developed for use in converting biomass-derived sugars into sugar alcohol products. The sugar solution contaminant levels tested were based on the compositions of enzymatic hydrolysis product from wheat millfeed and acid hydrolysis product from dairy manure solids. In both cases the sugars were relatively dilute. In the case of enzymatic hydrolysis of the millfeed, the sugar was primarily glucose from starch in the product solution. The manure was processed at two levels of severity to produce either a mixed xylose and glucose solution or a primarily glucose solution, as derived from mainly the hemicellulose or the cellulose, respectively.

A 300-mL Parr bomb reactor was operated in a semi-batch mode wherein hydrogen pressure was maintained and multiple liquid samples were removed over the 6-hr period of the test. The sugar-water solution feedstock and catalyst particles (3 wt% ruthenium metal on rutile titania) were stirred in the reactor, which was maintained at constant temperature (100°C) and hydrogen over-pressure (8.3 MPa). The product liquids were analyzed by high-pressure liquid chromatography (HPLC) using a conventional carbohydrate column (Bio-Rad Aminex HPX-87H, 300 x 7.8 mm,) at 65°C with a 5 mM sulfuric acid mobile phase (isocratic), at a flow rate of 0.6 ml/min and a refractive index detector. Column calibration was maintained by continual analysis of standard compounds. Analysis of the products showed, in most cases, a very high selectivity to the sugar alcohol product. Traces of hydrogenolysis products (lower molecular weight polyols) were noted, as were trace yields of methane and carbon dioxide. Glucose (or xylose) conversion is typically reported here based on reduction of sugar concentration, with time zero at temperature being the point when heat-up of the reactor raised the aqueous temperature to 100°C.

The non-sugar components in the hydrolysates were determined to be a collection of metals, anions, and nitrogenous material. The inorganic elements (Ca, K, Mg, Na, S, P, Al, Si) were measured by inductively coupled plasma-optical emission spectrometer (ICP-OES). Dissolved ammonium was measured with an ion selective electrode.

The ICP was a Perkin-Elmer 3000DV with an AS90 Autosampler, which has an instrument detection limit of about 1 ppb (for most elements) with a linear calibration up to 100 ppm (for most elements). Solid samples were prepared via microwave digestion in concentrated nitric and hydrochloric acids, then diluted to volume. The ICP was calibrated and verified with two independent certified standard sets. Spikes and dilutions were done for each batch of samples to check for and/or mitigate any matrix effects. The ICP process ran a constant pump rate of 1.5 ml/min for all samples and standards during analysis. A 3 ml/min rinse and initial sample flush was used to switch between each sample and standard. The plasma was run at 1450 W with argon flow. Trace metal grade (sub-ppb) acids and two independently NIST-certified calibration standard sets were used for calibration and method verification.

Anions, including chloride, were measured by ion chromatography (IC) using a Dionex DX 500 IC consisting of a GP40 Pump, EG40 Eluent Generator, ED40 Electrochemical Detector, with an AS3500 autosampler. An ASRS-Ultra 4 mm suppressor was used (at 100 mW) to minimize baseline drift. The chromatography was performed using an AG-11 guard column and an AS-11HC column running at 30°C with an hydroxide gradient from 0.5 mM to 41 mM and a flow rate of 1.2 ml/min. Certified standards were used to calibrate the IC.

Results and Discussion

The experimental results are presented in several groups. The tests in the first group were performed with contaminant-free sugar solution to provide a baseline for comparison with the tests involving contaminants. The second group provides an overview of the range of the tests performed. The subsequent groups are more elaborate collections to evaluate certain contaminants perceived to be of greatest significance.

Sugar hydrogenation studies

The tests to quantify the reaction rate and its reproducibility used reagent glucose (5 wt%) in deionized water as the feedstock. The test was repeated to evaluate the reproducibility of the reactor system. The glucose solution was also tested at two other concentrations, 2.6 wt% and 7.4 wt%, to evaluate the effect of concentration. The results of these tests are depicted in Figure 1. Overall, these results show the range of variability achieved with this test. The glucose conversion curves show a slight trend of increased rate of glucose conversion at lower concentration. In all cases, the glucose conversion reaches 95% within 2 h at temperature.

Figure 2 shows the sugar hydrogenation and sugar alcohol production over the time of the tests for comparison of glucose and xylose. Clearly, the xylose is hydrogenated more readily. These tests at higher concentrations of sugars show a concentration effect in the glucose case, but not in the xylose case, as the reaction is so rapid that the concentration appears to have little impact. High selectivity (85% to 95%) to the sugar alcohol product is seen in all cases.

In another test with a mixed solution of 10% glucose and 10% xylose (20% total concentration), the interaction of the two sugars does not appear to occur. Figure 3 shows conversion curves for both glucose (signified by diamonds) and xylose (signified by squares).

As seen, the xylose reaction is very fast at either 10% or 20% concentration and at essentially the same rate with 10% glucose added to 10% xylose. The glucose reaction rate is reduced slightly by the competition of the 10% xylose, but not nearly as much as with the addition of the extra 10% of glucose, which reacts more slowly.

Trace contaminant studies

Based on the analyses of the trace contaminants conducted on the wheat millfeed-derived products, numerous potential problem components were identified, relative to catalyst activity (3). These components (shown in Table 1) include sulfate (potential for metal sulfide formation); calcium, magnesium, and phosphate (potential for catalyst pore plugging by insoluble salt precipitation); sodium or potassium (alkali attack on the catalyst support); organic nitrogen components, such as amino acids (thiol source for metal sulfide formation), proteins (pore plugging by precipitation of denatured forms) or urea (metal complex formation); chloride (reaction with the metal); phytic acid or sodium phytate (decompose and precipitate as phosphate); and maltose and maltodextrins (pore plugging or catalytic site plugging).

Tests were completed with added reagent chemicals (identified in Table 1) to model the various trace contaminants and, consequently, identify any cause of catalyst inactivity. The results of the tests of glucose hydrogenation with these components added are summarized in the far-right column of Table 1. In this series of tests, no component was identified as the offending material. The components had insignificant effect on either the rate of reaction or the total conversion achieved in the tests. The inorganic components were added as salts to the feedstock solution, as noted in the table. The phytic is a phosphorylated cyclohexanehexitol, which is found in wheat. It had no effect in either the acid or sodium salt form. In addition to the inorganic component results, the carbohydrate structures also appeared to have little effect on

activity. The nitrogenous materials were the one component, that may not have been adequately modeled in these tests (3).

Only the cysteine showed a deactivation of the catalyst; however, its deactivation was not reversible (by water wash of the catalyst), a characteristic of the wheat-derived material (3). Therefore, we concluded that the cysteine deactivation was not analogous to the deactivation caused by wheat millfeed hydrolysates. Although cysteine is identified as a component of wheat protein structures, it is not likely to be found as cysteine in the hydrolysis products. More likely, it would be present as the bridged disulfide, cystine, following the oxidative reactions in the processing. As cystine, there is no free thiol available to react with the catalyst metal and, therefore, no mechanism for catalyst deactivation. As seen in Table 1, the addition of cystine had no effect on the glucose hydrogenation.

A subsequent series of glucose tests (10% concentration) were performed with added acids and bases to model expected anion and cation contaminants from manure hydrolysates (see Figure 4). The contaminants were added at 100 ppm. The ammonium (added as carbonate) shows a decided inhibition of the catalysis. Calcium (added as carbonate) has a mild effect and the nitric acid contaminant even less, nearer the range of experimental variation. The potassium (added as carbonate) effect is negligible (within experimental variation), as is the effect of the other acids.

Manure hydrolysate model contaminant tests

Additional tests with added acids and bases were also performed to more accurately model expected anion and cation contaminants from manure. The results are shown in Figure 5. The contaminants were added at the levels noted in the key, based on expected values in manure-derived feedstocks. The ammonium compounds show a decided inhibition of the catalysis at this

higher concentration, especially when added as carbonate but also to a lesser degree in the hydroxide form. Calcium (added as carbonate) has a mild effect. Neither the magnesium nor the potassium bases nor the calcium sulfate appear to have an effect at these concentrations.

A shorter companion series of tests was performed with xylose as the feedstock. As shown in Figure 6, ammonium carbonate also inhibits the xylose hydrogenation. However, while the xylose hydrogenation is noticeably faster than the glucose hydrogenation, the effect of the ammonium carbonate is less in the xylose case as compared to the glucose. The calcium carbonate appears to have almost no impact on the xylose hydrogenation at these concentrations.

Ammonium ion detailed studies

The ammonium carbonate inhibition was further studied with glucose to evaluate its scale of effect over a range of concentration. As seen in Figure 7, the inhibition of the glucose hydrogenation is a reproducible effect and is directly proportional to the concentration of the ammonium carbonate. Consequently, if the higher concentration of ammonium is present in the manure-derived feedstocks, there likely will be a significant effect on the rate of hydrogenation of the glucose. Also noted at the higher concentrations was the competitive reaction of isomerization of the glucose to form fructose. Correlating with this production of fructose is a reduction in the sorbitol product. As a result, the true inhibition of the glucose hydrogenation is even more severe than suggested by Figure 7.

Additional tests with ammonium compounds were performed to address the effect of ammonium ion (see Figure 8). It is clear that the catalyst inhibition was not based only on the presence of ammonium ion. Ammonium carbonate showed the largest inhibition of the glucose hydrogenation reaction, while chloride and hydroxide had lesser effects. The ammonium nitrate caused no apparent inhibition on glucose conversion. A similar lack of effect was shown with

potassium nitrate. In the case of the ammonium nitrate, the glucose conversion mechanism was affected, so that the sorbitol yield was reduced by about 20%, but numerous byproducts and overreaction products (lower molecular weight polyols) were evident.

Calcium ion detailed studies

The effect of calcium is not so straightforward. As seen in Figure 9, calcium carbonate concentration appears to have little effect on the extent of inhibition of the glucose conversion, which is low, and is about the same in all cases, i.e., from 100 to 5300 ppm. Calcium hydroxide appears to have no inhibitory effect.

Comparative catalyst tests

Contaminant poisoning of the catalyst is likely to be catalyst specific. To evaluate this parameter, comparative tests of the ruthenium catalyst were made with a more conventional nickel catalyst (50% Ni metal on high-surface area alumina). Figure 10 shows glucose conversion comparisons for two catalysts. The ruthenium and nickel catalysts exhibit similar activity in this batch test. However, although reaction inhibition was seen with the ruthenium catalyst in the presence of the ammonium carbonate (0.056M NH_4^+), there was much less severe reaction inhibition when using the nickel catalyst in the presence of ammonium carbonate. There was also reaction inhibition seen with the ruthenium catalyst, with addition of calcium carbonate (0.0025M Ca^{++}), but the inhibition was not significant when using the nickel catalyst in the presence of the same amount of calcium carbonate.

A model manure solution was prepared based on 10% glucose (as a carbohydrate hydrolysate model) with the various mineral components. The model solution was processed with three different catalyst formulations for comparison. The two nickel catalysts, ruthenium-

stabilized and copper-stabilized (4), exhibited no effects from the contaminants, while the ruthenium showed reduced activity similar to that noted above.

Detailed sulfate and ammonium tests

Initial analyses showed that the manure hydrolysis feedstocks were relatively dilute (~1% sugars) and mainly consisted of xylose when hydrolyzed at low temperature (~100°C). The sulfuric acid remainder from the hydrolysis can be significant. Hydrogenation tests with manure acid hydrolysates showed slow reaction rates in all cases, suggesting a large inhibition of the catalytic chemistry. Model tests were performed with 1% xylose in water with a range of sulfuric acid, from 0 to 6 wt%, to test the effect of the residual acid from the hydrolysis treatment. The results, depicted in Figure 11, showed that sulfuric acid has only a minor effect on the catalytic chemistry, noticeable only at the highest concentration tested and much too small to explain the results of the manure-derived feedstocks.

Analysis of ammonia performed on the manure hydrolysate samples showed ammonia concentrations of about 1300 ppm in the low-temperature acid hydrolysates and about 400 ppm in the moderate-temperature (135°C) acid hydrolysates. As reported above, model tests of ammonia at this concentration range appear to show little or no effect. The sulfuric acid remaining in the samples from the hydrolysis ranges from 1 to 8 wt%. Again as reported above, tests of sulfuric acid in the range of the hydrolysates also appear to have only a minor effect. A combination of the two (ammonia and sulfuric acid) might explain the catalyst inhibition. Table 2 summarizes these results. No significant effect on xylose hydrogenation is apparent at any of these sulfate concentrations with a clean xylose feedstock. The addition of ammonia with or without sulfate present also does not appear to affect on xylose hydrogenation in a clean solution.

Tests with peptone contaminant

One impurity in the manure hydrolysates is the protein-derived material, and peptone was added to the glucose solution to model the hydrolyzed protein material. Figure 12 shows a peptone-concentration-dependent effect on the rate of glucose hydrogenation. As the peptone addition was increased from 0.1 g to 1 g and to 5 g, glucose hydrogenation was slowed to the point that only a partial conversion was achieved after the full 6 h test compared to nearly complete conversion achieved in 2 h with reagent glucose alone. In addition, the reduction in rate of glucose hydrogenation is in the same range as that found in processing of the actual manure hydrolysates. The amount of peptone results in nitrogen contents similar to that found in the manure hydrolysates.

Catalyst washing tests

Another important issue is the permanence of the catalyst inhibition or poisoning. The permanence of catalyst inhibition is dependent on the mechanism of the chemical interaction of the poison with the catalyst. The catalyst inhibition and the resulting reaction rate reduction could result from competition between the poison and the preferred reactant at the catalytic site, either because of a high affinity of the poison for the catalyst site or because of its slow reaction once on the catalyst site. If the affinity is too high, as when the poison actually reacts with the catalyst to form a new compound, the catalyst is permanently poisoned. If the inhibition is only related to a slow rate of reaction, it may be possible to remove the poison from the catalyst surface and restore catalyst activity.

Catalyst-washing tests were performed to determine if catalyst activity could be recovered (see Figure 13). Catalysts used in hydrogenation tests with manure hydrolysates were washed with water and reused to hydrogenate reagent glucose. The two high-temperature

hydrolysates, designated solution A and solution B, gave low rates of conversion of glucose when hydrogenated directly as produced. The catalysts from those two tests, after washing, showed much improved reaction rates, approaching that of unused catalyst.

This reversibility of the poisoning is an important parameter. Two of the catalysts exhibiting inhibited activity shown in Figure 8 were also tested following a water wash to determine the permanence of the deactivation. In the test results shown in Figure 14, it is apparent that the catalyst deactivation noted in an initial test can be reversed by the water wash, and the catalyst activity can be returned to a level at or near that of unused catalyst. The effect was demonstrated for both ammonium carbonate and ammonium hydroxide.

Additional washing tests with the peptone-poisoned catalysts showed a similar relationship. As seen in Figure 15, the washed catalysts showed greatly improved activity compared to the result initially with the peptone-contaminated environment. It appears that the water washing of the catalyst improved the activity equivalent to an order of magnitude reduction in the peptone contamination. However, in this case, there is not a total recovery of catalyst activity to the pre-contaminated state. This recovery of activity indicates that a significant portion of the catalyst deactivation results from a competition of the peptone or peptone-derived material (Maillard condensate) with the glucose for the catalytic site. In addition, also illustrated in these results, is that a second wash does not improve the activity any further. This result appears to verify a combined effect of competition for the catalytic site with a more permanent poisoning of the catalytic site by the peptone.

A common thread that can link the ammonium and peptone catalyst poisoning results described above could be the Maillard reactions of amino acids with sugars (5). Recent studies have shown that the ammonium ion is highly reactive, more so than substituted versions (6). Its

use as ammonium bicarbonate in developing flavoring compounds by Maillard reactions in extrusion cookers has been reported (7). It is likely that such reactions could occur at our processing conditions. We can speculate that such products could have acted as catalyst surface poisons, which might have been subsequently washed from the catalyst, before it was reused in its active form.

Conclusions

Reaction rates for aqueous phase catalytic hydrogenation will vary with different sugars. The C5 sugar, xylose, reacts more readily than the C6 sugar, glucose. However, these tests show processing mixed sugars does not adversely affect the catalytic hydrogenation.

Some biomass-derived contaminants, on the other hand, may affect the catalytic processing rate. Ammonium shows significant inhibition; calcium may also have an effect. Potassium, though, appears to have too little interaction to be noticeable at the concentrations tested. The common acid anions phosphate, sulfate, and chloride appear to have no effect, while nitrate changes the conversion route and the product slate through a sugar isomerization mechanism. These tests show while some contaminants may affect the catalytic processing rate, most have no impact, and there is no indication of a combinatorial effect on the catalyst when several of the contaminants are present in the feedstock. Consequently, the calcium and ammonium continue to be the key components of concern. However, the fundamental mechanism of these inhibitions is not known at present.

Peptone (hydrolyzed protein) appears to best mimic the catalytic inhibition experienced in the catalytic hydrogenation of sugars in manure hydrolysate solutions, suggesting that the inhibitory effect is due to hydrolyzed protein in the solution. The inhibitory effect appears to

stem from a combination of mechanisms, probably related to Maillard-type reactions forming condensed structures, which can block active catalyst sites. Some activity can be regained by simply washing the used catalyst with water. Thus, the suggested catalyst “poisoning” is more accurately an equilibrium competition effect or a site blocking. However, the washed catalyst does not totally regain its original activity level, suggesting there is also a more permanent poisoning in this case.

Acknowledgements

The authors wish to acknowledge their collaboration with the Biological Systems Engineering Department of Washington State University, specifically, Prof. Shulin Chen and his graduate students, Wei Liao and Chaunbin Liu, who produced the manure solids hydrolysate solutions. The testing and analyses described here were performed at the Pacific Northwest National Laboratory operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RL01830.

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Table 1.
Testing Results with Trace Contaminants in Glucose

Contaminant	Form Tested	Amount Tested, ppm	Amount in Wheat Millfeed Hydrolysate, ppm	Reduction in Reactivity
Sodium	sulfate	1000	18	None
Calcium	hydroxide	100	77	None
Magnesium	hydroxide	400	209	None
Potassium	sulfate	1050	1050	None
Phosphorus	phosphoric acid	950	510	None
Phosphorus	phytic acid	430	510	None
Phosphorus	dodeca-sodium phytate	550	510	None
Sulfate	sodium sulfate	1000	1050	None
Chloride	sodium chloride	49	56	None
Kjeldahl N	urea	470	425	None
Cysteine	l-cysteine	200	200*	95-99%
Cysteine	dl-cystine	200	200*	None
Maltose	crystalline	10,000	3000	None
Maltotriose	crystalline	10,000	2000	None
Glucose oligomer	maltodextrin 13-17	10,000	NA	None
Glucose oligomer	maltodextrin 4-7	10,000	NA	None

* based on wheat analysis, amount in hydrolysate not analyzed

Table 2.

Model Compound Xylose Hydrogenation Results

			Batch Feed		6 hr	
	Ammonium,	Sulfate,	Xylose	Sulfate	Xylose	Xylitol
	ppm	%		(area)	Conversion	Yield
No additives	0	0	0.471	0	98%	78%
Low NH ₄ OH	445	0	0.471	0	98%	92%
Low (NH ₄) ₂ SO ₄	488	0.1	0.471	202999	100%	78%
Low (NH ₄) ₂ SO ₄ + H ₂ SO ₄	398	4.6	0.471	7583905	98%	89%
High NH ₄ OH	1258	0	3.94	0	99.3%	79%
High (NH ₄) ₂ SO ₄	1370	0.4	3.94	617589	99.8%	92%
High (NH ₄) ₂ SO ₄ + low H ₂ SO ₄	1524	1.5	3.94	1815351	99.8%	99%
High (NH ₄) ₂ SO ₄ + H ₂ SO ₄	1258	7.1	3.94	12429875	99.7%	82%

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Fig. 5. Glucose conversion inhibition by manure model contaminants.

Fig. 6. Xylose conversion with contaminants.

Fig. 7. Glucose conversion with ammonium present.

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Fig. 12. Glucose conversion with addition of peptone.

Fig. 13. Comparison of catalyst activity with raw hydrolysates and after washing.

Fig. 14. Glucose conversion with reused catalyst.

Fig. 15. Effect of washing peptone-contaminated catalysts.

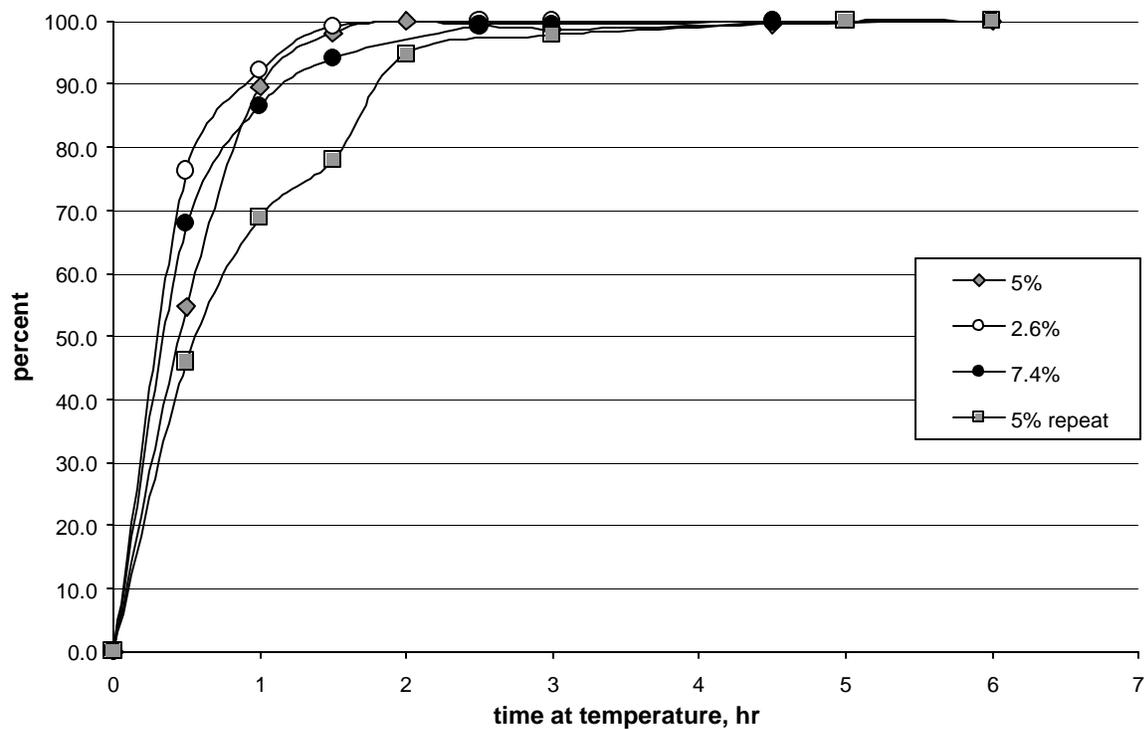


Fig. 1. Glucose conversion by catalytic hydrogenation at 100°C

Fig. 2. Sugar conversion to sugar alcohol at 100°C.

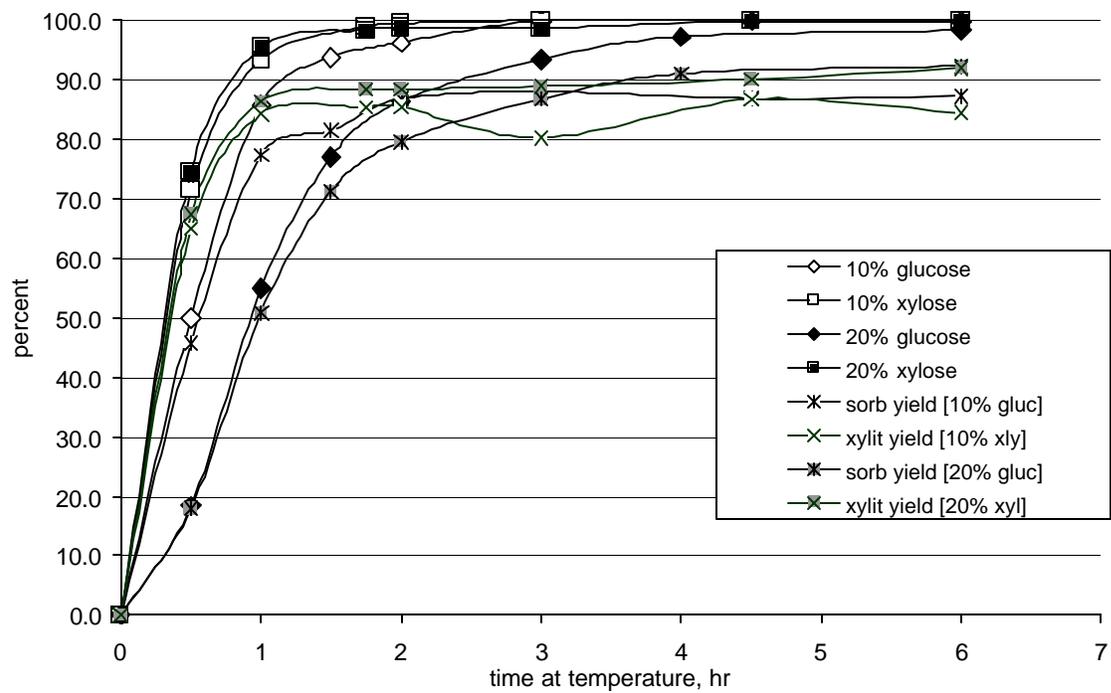
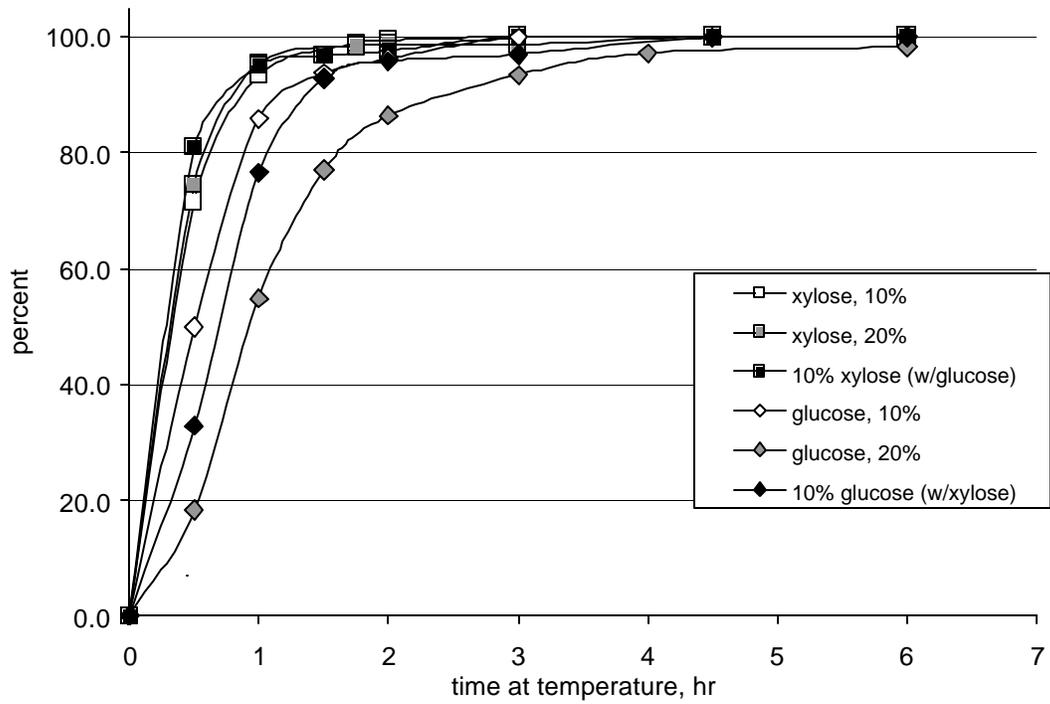


Figure 3. Glucose/Xylose conversion.



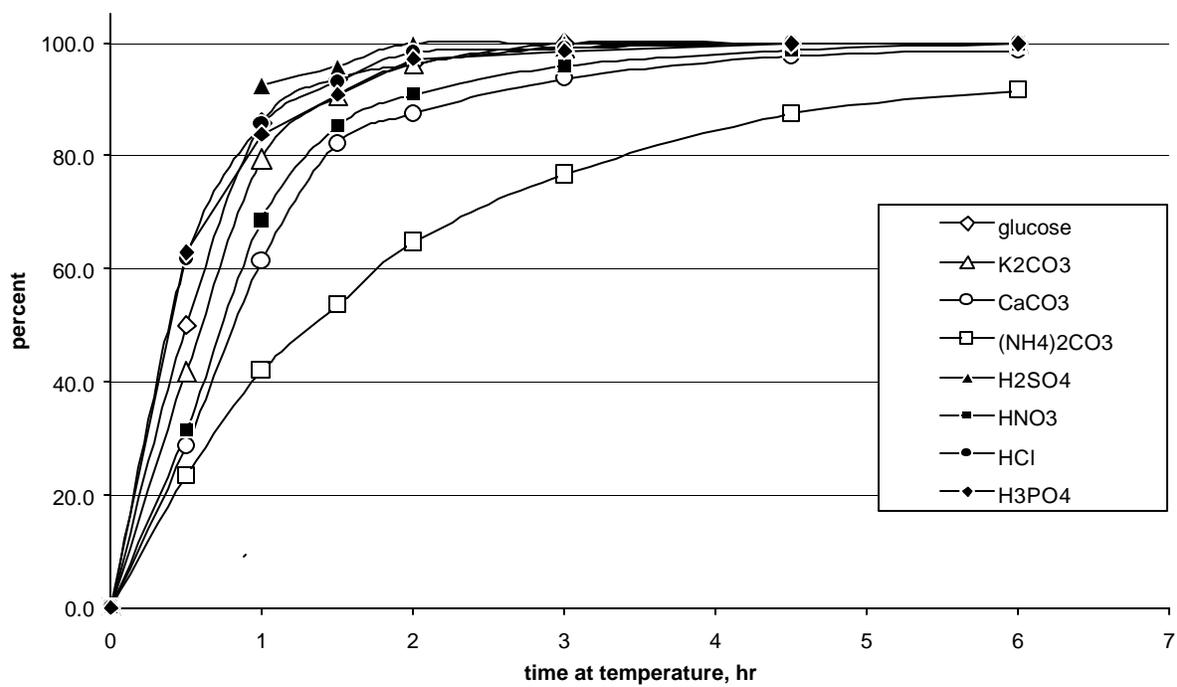


Fig. 4. Glucose conversion in the presence of inorganic contaminants

Fig. 5. Glucose conversion inhibition by manure model contaminants.

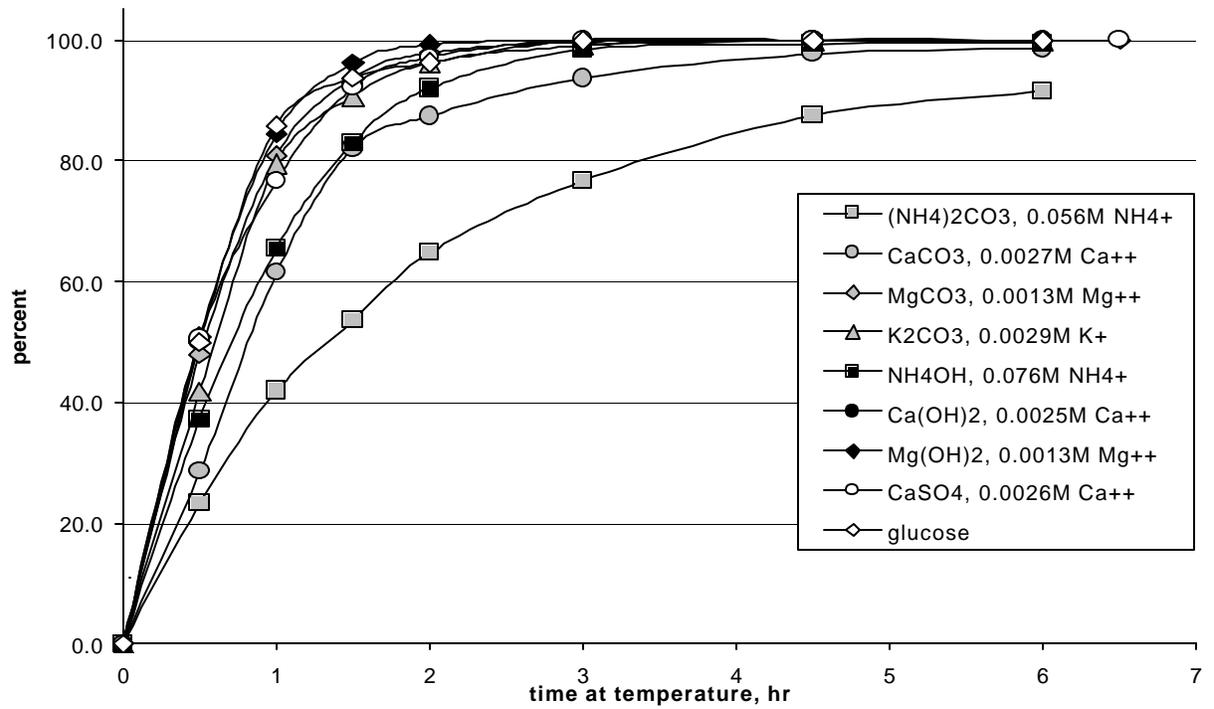


Fig. 6. Xylose conversion with contaminants.

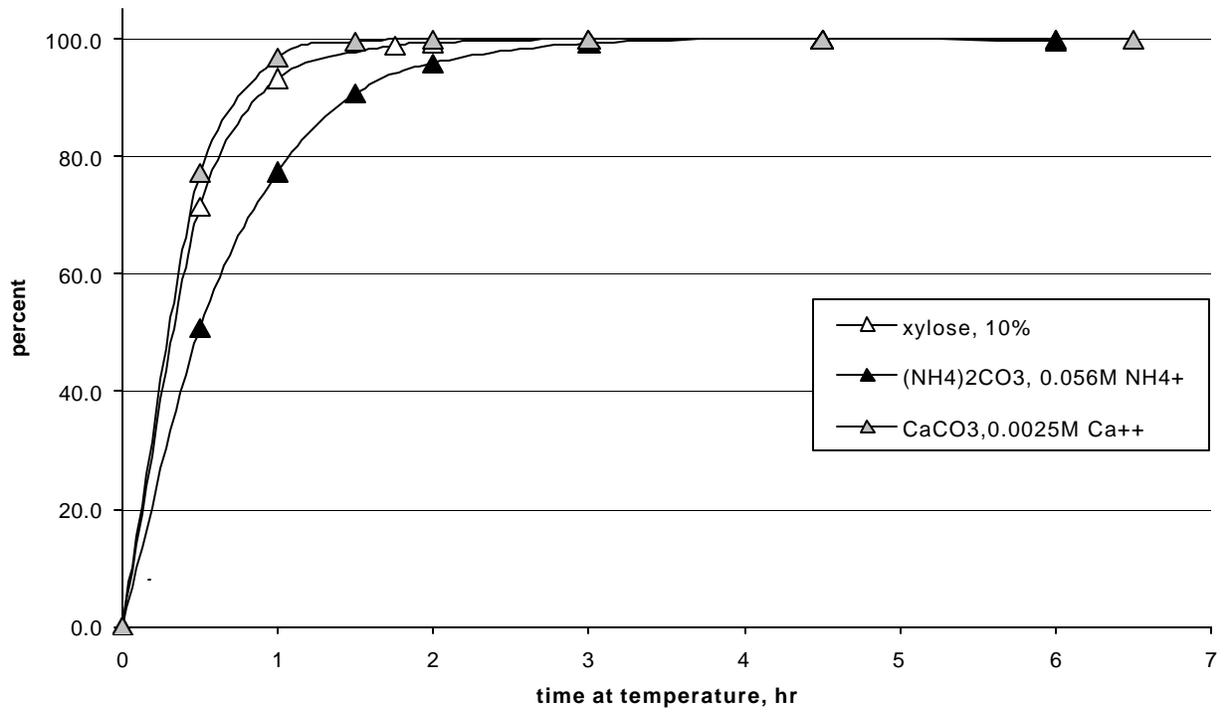
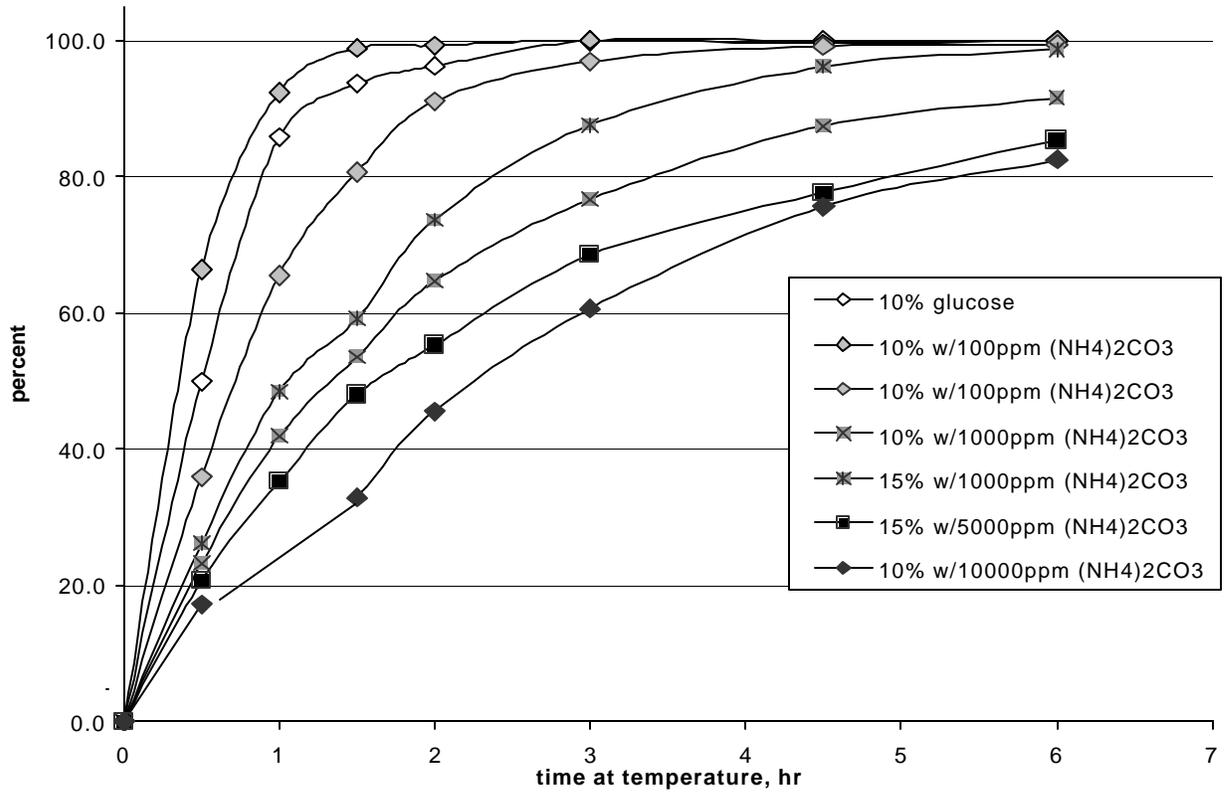


Fig. 7. Glucose conversion with ammonium present.



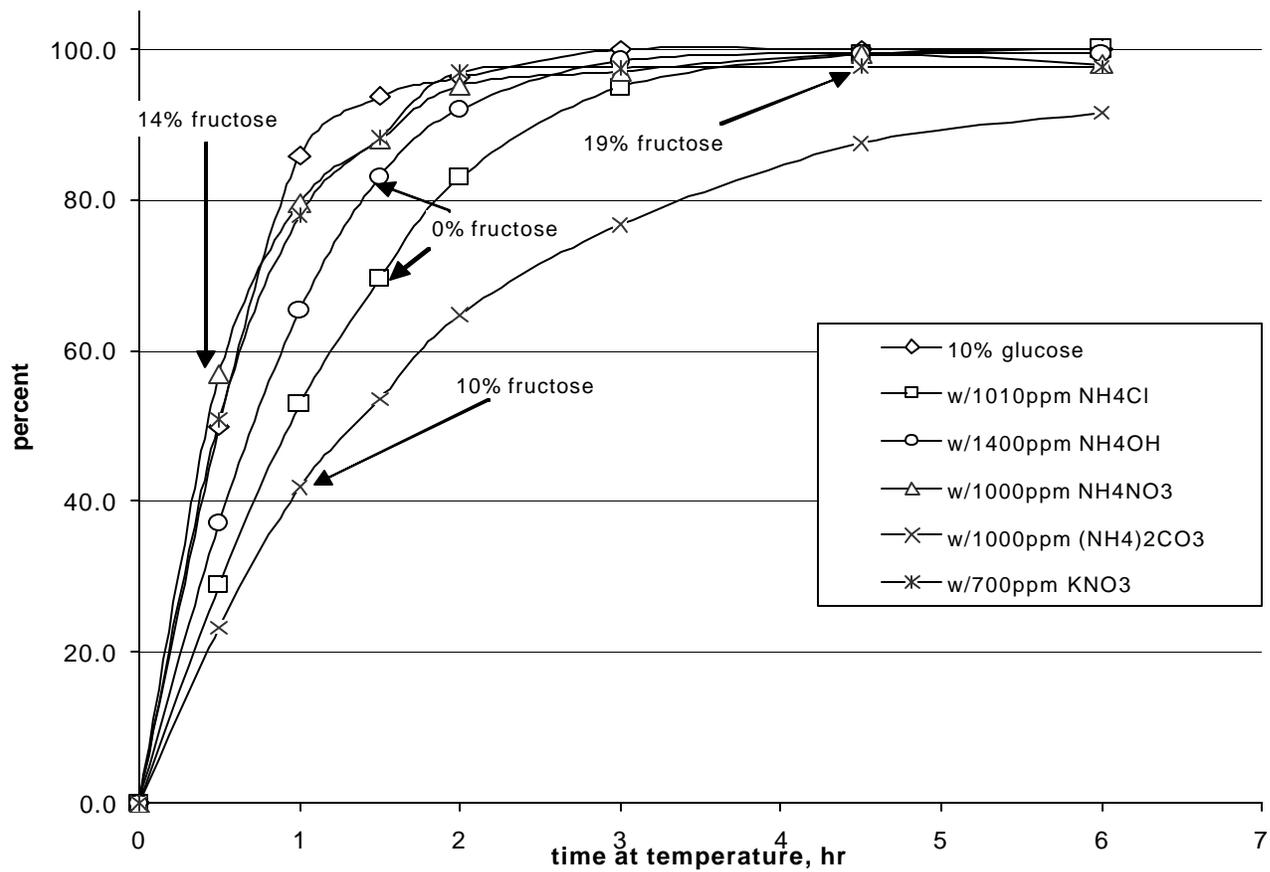


Fig. 8. Glucose conversion with ammonium and nitrates.

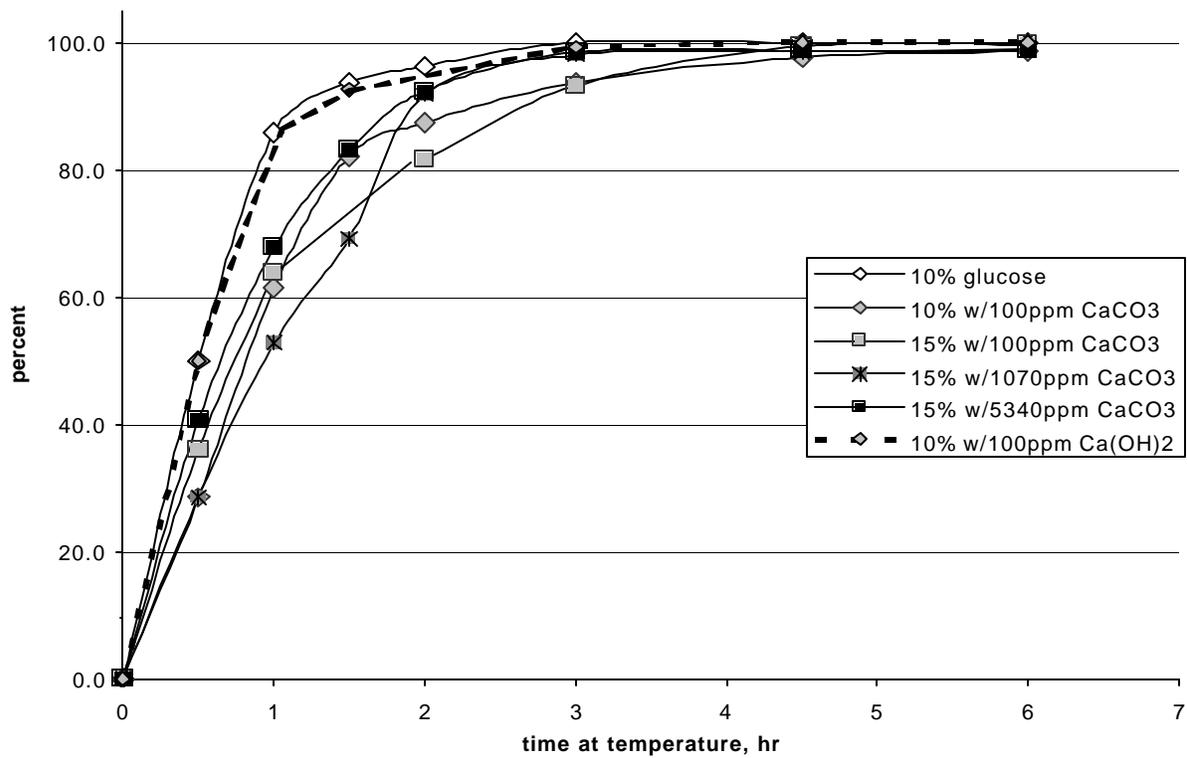


Fig. 9. Glucose conversion with calcium present.

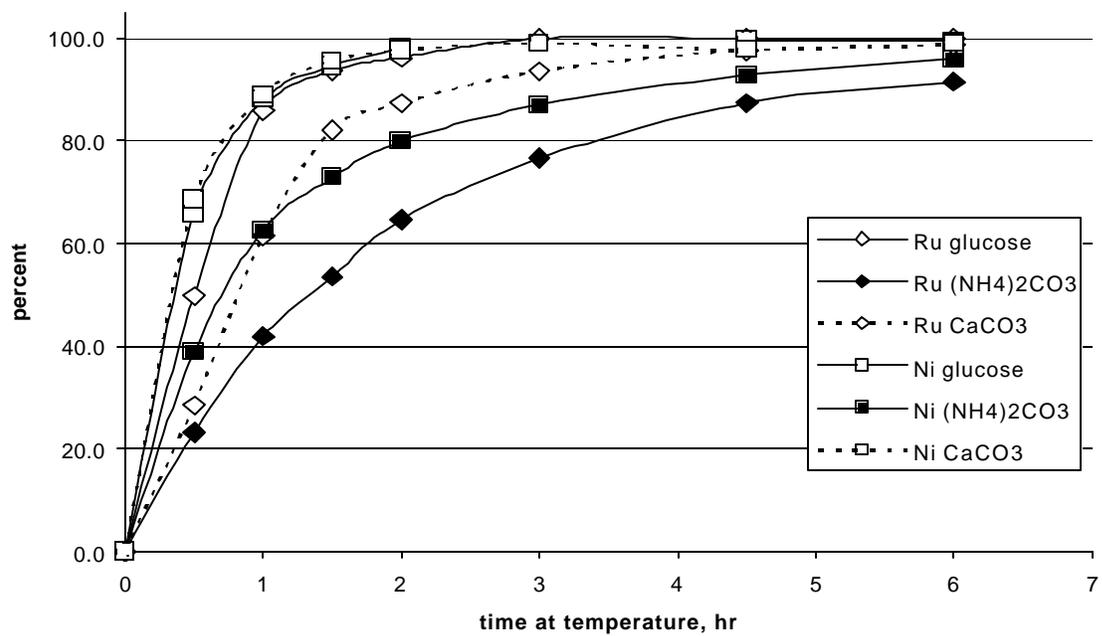


Fig. 10. Glucose conversion with different catalysts.

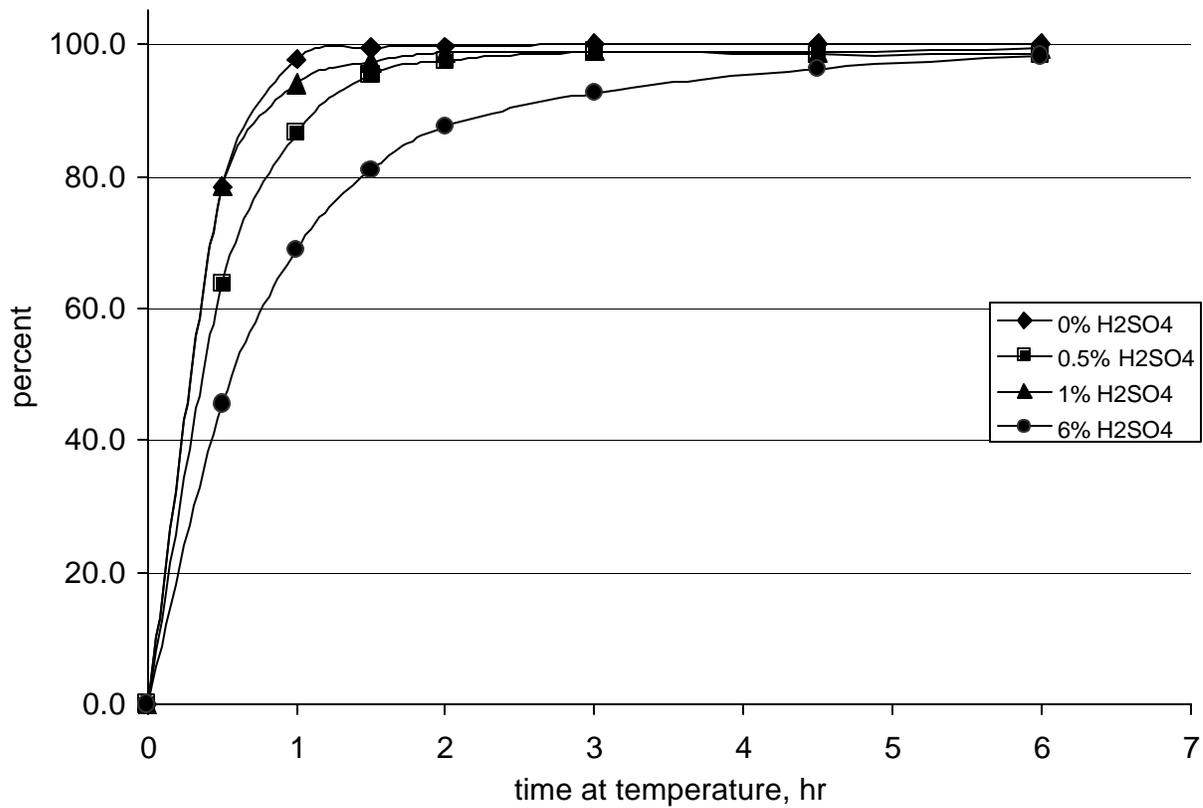


Fig. 11. Xylose (1%) conversion with sulfuric acid.

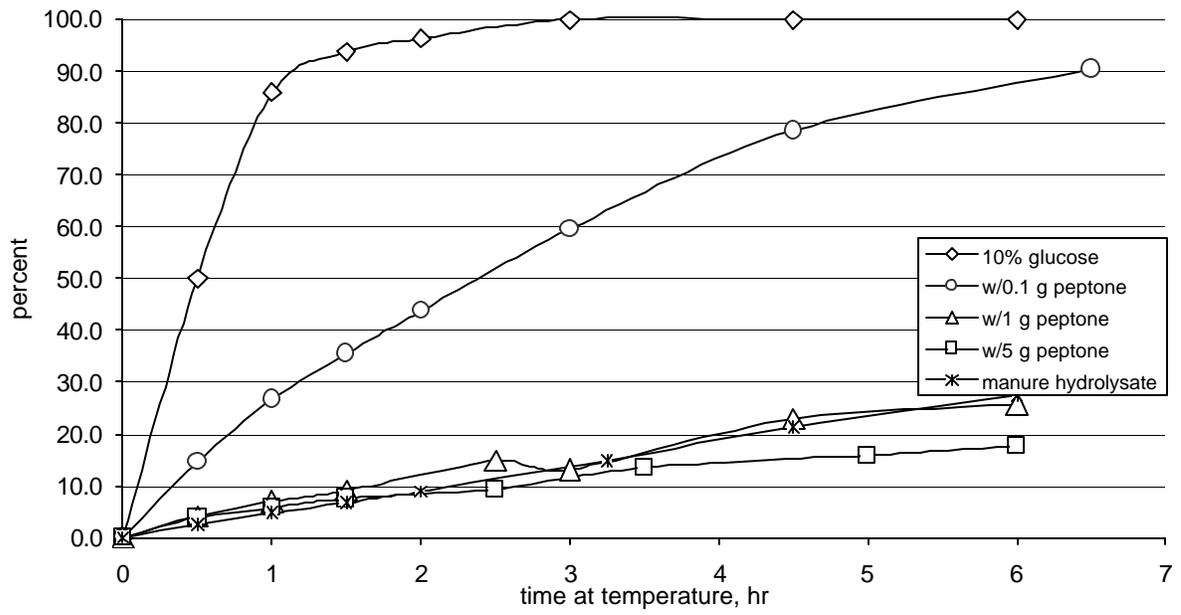


Fig. 12. Glucose conversion with addition of peptone.

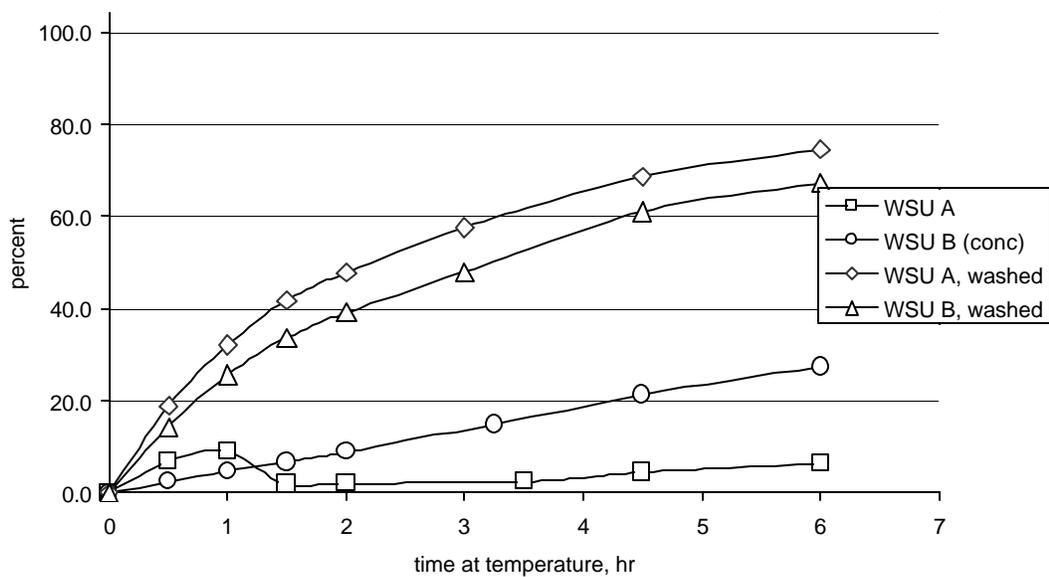
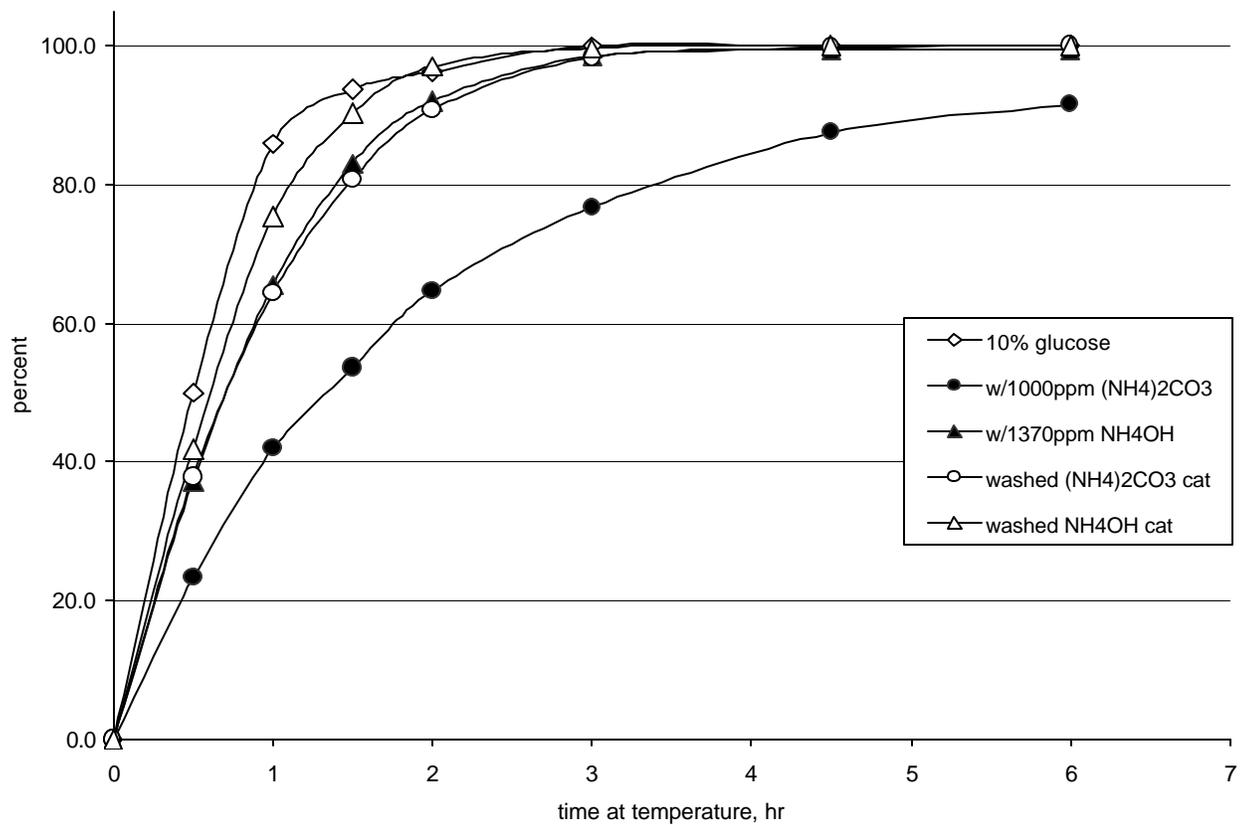


Fig. 13. Comparison of catalyst activity with raw hydrolysates and after washing.

Fig. 14. Glucose conversion with reused catalyst.



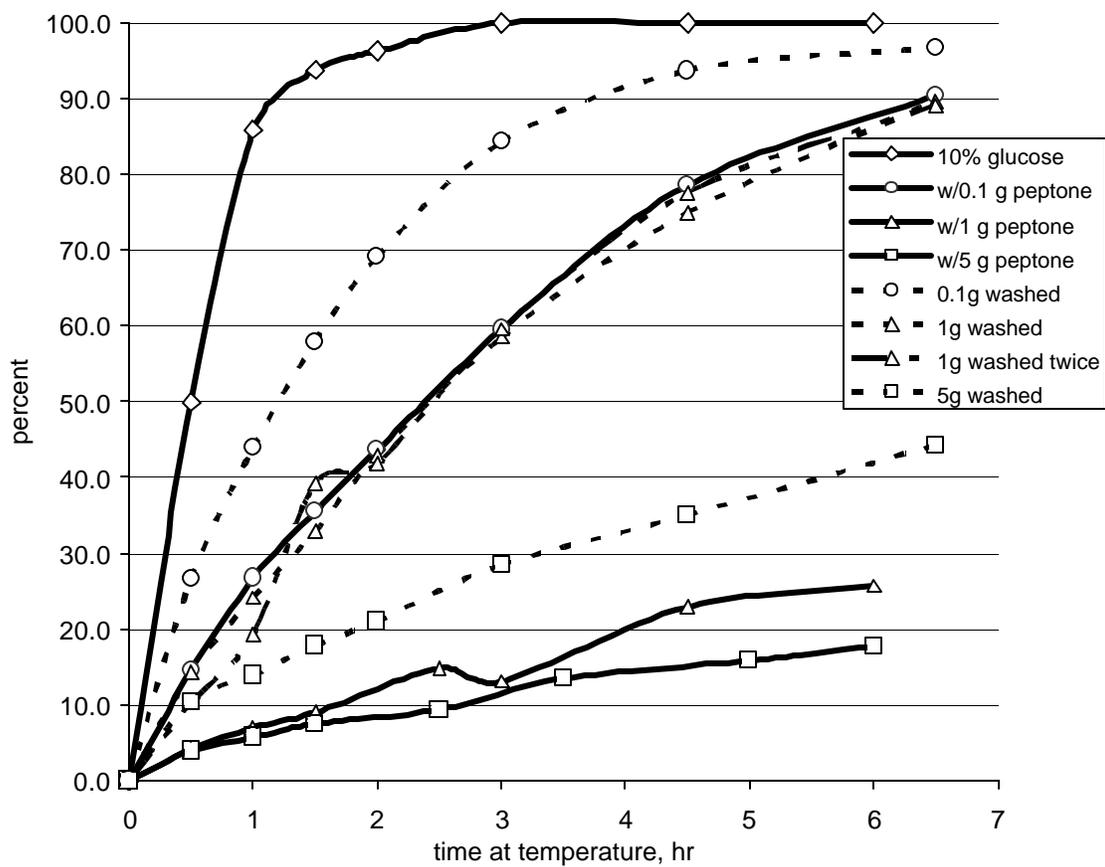


Fig. 15. Effect of washing peptone-contaminated catalysts.