FUELS AND CHEMICALS FROM CORN

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ABSTRACT

New conversion chemistries for deriving valuable products from corn processed by wet milling are discussed. Product targets have been established because of the potential economic attractiveness and synergistic fit with existing corn wet milling infrastructure. Selected products that meet these criteria include polyols and derivatives of diammonium succinate.

INTRODUCTION

The US currently produces about 10 billion bushels of corn annually, with 20%, or 2 billion bushels, processed by either wet or dry milling. Approximately 550 to 600 million bushels of the processed corn are used to produce ethanol. The remainder is processed to produce food and non-food products.

While corn wet milling has been practiced since the mid 1800's, technology advancements have continued to improve processing efficiency and bring about a substantial reduction in water usage and energy requirements. The corn wet milling process consists of seven major unit operations: 1) corn cleaning and inspection, 2) steeping, 3) grinding, 4) germ separation, 5) fiber separation, 6) starch and protein separation and 7) downstream processing.

The major components from corn wet milling include corn oil (1.5 lb/bu), corn gluten meal (2.6 lb/bu 60% protein), corn gluten feed (13.5 lb/bu-20% protein), and starch (32 lb/bu). Corn oil is extracted from the germ, refined and used to produce finished oil. Combining the fiber fraction with steep water, which is followed by drying and sold primarily as animal food, produces corn gluten feed. Corn gluten meal is derived from the protein fraction, and also is sold as animal food. Starch is recovered and converted by several processes to produce various starch products. Starch also is hydrolyzed enzymatically and used as a feedstock to produce products such as high fructose corn syrup, ethanol, lactic acid, lysine, citric acid and a variety of other fermentation products. However, through further technology advancements, additional valuable products can be derived from corn processing operations.

We will discuss specific products/processes currently under development, such as reaction chemistry for converting xylitol to polyols and converting fermentation derived diammonium succinate to pyrrolidones. Product targets have been established because of the potential economic attractiveness and synergistic fit with the existing corn wet milling infrastructure: products derived from corn fiber; polyols from 5 carbon sugars; and derivatives of succinic acid and diammonium succinate (DAS). Economics associated with value added products from corn are addressed and a brief discussion on current products is included.

FEEDSTOCK COSTS

The major feedstock from corn wet milling to be utilized for the production of fuels and chemicals is starch. Starch costs are estimated at $0.05 to 0.06 per pound. The cost of starch is based on the overall corn wet milling process and the coproduct value associated with the oil, corn gluten feed and corn gluten meal. The actual starch cost depends on both the specific corn wet mill and the mill size. Corn pricing has remained constant during the past several decades. The average annual corn price over the past 10 yrs has been $2.37/bu.

The fiber fraction of corn (5.5 lb/bu) is another feedstock opportunity that could represent a source of 5 carbon sugars, xylose and arabinose, at a very low cost. Corn fiber is currently sold as part of corn gluten feed, and the value of the feed is on the order of $0.05 per pound. The real value in corn gluten feed is the protein and fiber primarily is used as a carrier for the protein.

FUEL AND CHEMICALS FROM CORN (POTENTIAL PRODUCTS)

Through new advancements in producing chemicals from renewable feedstocks, opportunities for additional value added products arise. For example, new products are being derived from corn fiber. Furthermore, major area under development for reducing ethanol costs is based on utilizing the 5 carbon sugars, xylose and arabinose, derived from corn fiber. This could reduce the overall cost of ethanol and increase the yield/bu. A new major application of lactic acid is for the production of polymer materials, specifically polylactic acid or PLA. PLA offers the potential to be a very large end use for lactic acid with potential markets of more than 1 billion pounds.

VALUE ADDED PRODUCTS FROM CORN FIBER

The US corn wet milling industry currently processes enough corn to produce about 8.8 billion pounds of corn fiber annually. Corn fiber consists of starch, protein, hemicellulose, polyphenolics and ash. The major components of interest in the corn fiber for the production of fuels and chemicals are the starch and hemicellulose components.

The starch stream will be hydrolyzed and used as a feedstock for the production of ethanol. The hemicellulose stream will be hydrolyzed and used as a feedstock to produce both ethanol and polyols.

The production of polyols from xylose and arabinose is a 2 step process. The first step is the hydrogenation of xylose and arabinose to produce xylitol and arabinitol. The second step is the hydrogenolysis of xylitol and arabinitol to produce polyols, namely, ethylene glycol, propylene glycol, and glycerol. The primary target product is propylene glycol. The reaction chemistry for hydrogenating xylose is shown in Fig. 1.

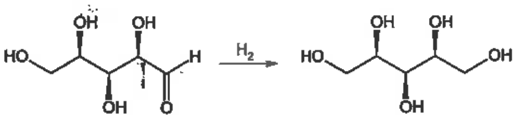

Figure 1. Hydrogenation of xylose to xylitol

The reaction chemistry for the conversion of xylitol to polyols, ethylene glycol, propylene glycol and glycerol is given in Fig. 2.

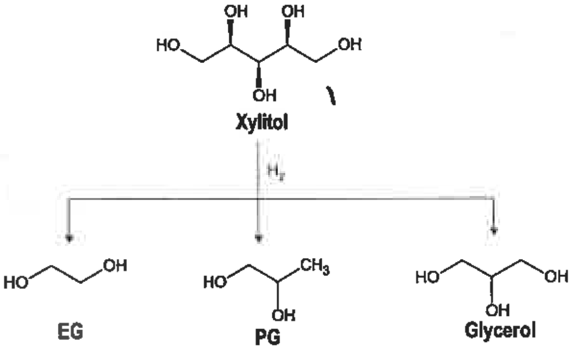

Figure 2. Reaction products from the hydrogenolysis of xylitol

Xylitol and arabinitol are produced from xylose and arabinose, respectively, by hydrogenation. Several catalysts including nickel and ruthenium can be used to carry out this transformation. Ruthenium supported on carbon affords the most efficient method for hydrogenation of xylose and arabinose. Selectivity of greater than 97% is obtained with a conversion approaching 100% in a continuous reactor system.

A variety of supported metal catalysts can be used to carry out the hydrogenolysis of xylitol to produce polyols. These metals include nickel, ruthenium, palladium and platinum. The metals are impregnated on an activated carbon support to maximize active surface area of the catalyst. The performance of these catalysts with respect to conversion and selectivity can vary depending on the carbon support, metal selected and operating conditions. The best current catalysts afford a total yield to desired products on the order of 80%.

Continuous reactor studies using the best catalyst as determined by batch experiments affords similar selectivities with conversions near 100%. Conversion and selectivity in the continuous reactor are influenced primarily by weight, hourly space velocity and temperature. One of the important features of the current catalyst is that overall selectivity is not compromised over a relatively wide range of temperatures. In addition, the selectivity to propylene glycol increases with increasing temperature due to the secondary conversion of glycerol to propylene glycol.

POLYOLS FROM 5 CARBON SUGARS

A novel catalyst formulation offers high selectivity and good conversion for the hydrogenolysis of xylitol to polyols. All studies were carried out with pristine xylitol; however, xylitol obtained from corn fiber via novel hydrolysis conditions performs in a similar manner. Continuous reactor studies are in progress to evaluate the potential catalyst lifetime. During 140 hrs on stream, there was no significant loss in activity with respect to conversion or selectivity. This is a critical issue for commercial deployment of the technology.

DERIVATIVES OF SUCCINIC ACID AND DIAMMONIUM SUCCINATE

Succinic acid can be produced by the fermentation of glucose. During fermentation, succinic acid must be neutralized to achieve reasonable concentrations. Typical final assays are 80 to 100 g/L. Fermentation rates are on the order of 1-2 g/L/hr. Products that can be produced from succinic acid include 1,4-butanediol, tetrahydrofuran (THF), and gamma-butyrolactone (GBL). The reaction chemistry is shown in Fig. 3A. The competitive route to all of these products is based on the maleic anhydride hydrogenation. Maleic anhydride is derived from the oxidation of butane over a vanadium catalyst. For a biobased route to be competitive economically with the petrochemical route, a new fermentation route must be developed that does not require neutralization. Neutralization of fermentation and subsequent conversion of the salt to the free acid require substantial capital and operating expenditures. As much as 40% of the overall operating and capital costs is associated with the purification and recovery of the succinic acid salt.

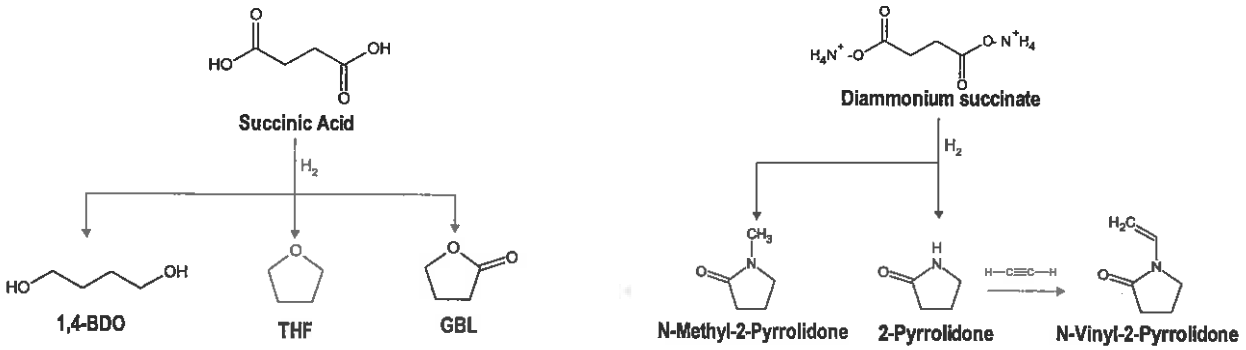

Figure 3A and B. Conversion of Succinic Acid and Diammonium Succinate to Various Commodity Products

In light of these economics, one strategy for deriving products from succinic acid fermentations is to identify products that can be obtained directly from the salts. One route that affords the economical production of chemicals from DAS is the formation of 2-pyrrolidone (2P) and N-methyl pyrrolidone (NMP). The reaction chemistry for these products is shown in Fig. 3B.

2-Pyrrolidone can be produced by the direct hydrogenation of aqueous DAS with hydrogen in the presence of an active metal catalyst. A mixed product of NMP and 2P can be produced from the conversion of DAS in the presence of methanol and an active metal catalyst. Results of converting aqueous DAS in the presence of methanol and hydrogen over a supported rhodium catalyst are shown in Fig. 4. Conversion for this reaction is near 100% with a NMP yield of 50% and a 2P yield of 30%. The remainder of the product is a polymer of 2P. In the early part of the reaction, there is formation of N-methyl succinimide, which converts to NMP as the reaction proceeds. Once 2P is formed it essentially remains during the course of the reaction.

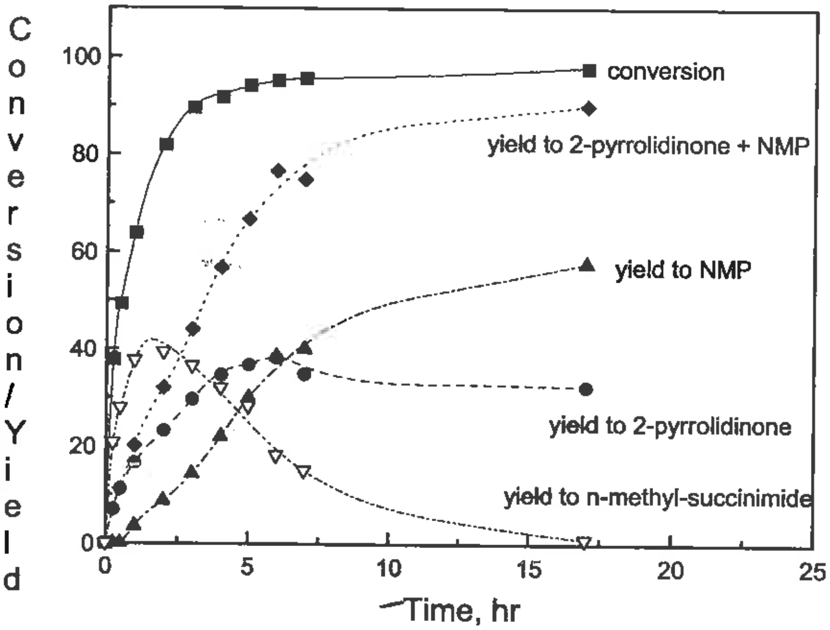

Figure 4. NMP and 2P Production Over a Rhodium Catalyst

NMP can be produced in a single stage reaction with DAS, hydrogen and methanol. The drawback of the single stage process is that a mixture of both NMP and 2P is formed. This mixture would require substantial separation costs to obtain a pure NMP product. Employing a 2 stage process, in which N-methylsuccinimide is formed first, prior to reduction, leads to near-complete conversion and selectivity to NMP (Table 1). The reaction was carried out at 1900-PSI hydrogen for the catalyst and temperature described. Pre-forming NMS is preferred to obtain high levels of NMP. Using the appropriate catalyst and reaction conditions, 100% NMP can be obtained when starting with NMS.

Table 1. Production of NMP from NMS

Catalyst Composition	Feedstock	Reaction Temperature	NMP +2P Yield	NMP:2P Ratio
2.5% Rh/2.5%Re/C	NMS	265 °C	54% (5 hrs)	5.3
2.5% Rh/2.5%Re/C	NMS	200 °C	89% (8hrs)	67.3
2.5% Rh/2.5%Zr/C	NMS	200 °C	81%	38.1

SUMMARY

The major driver for the production of chemicals from renewables is economics. Several parameters must be achieved to reach commercial success. The first and most obvious criterion is that substantial value must be created from the feedstock of choice. The second important criterion is that selectivity of the reaction sequence to the desired product must be high because of the direct impact on capital and operating costs. In addition, since most biobased feedstocks available are highly oxygenated, it only makes sense that the products contain oxygen as part of the structure. The production of polyols from 5 carbon sugars and the production of NMP from glucose afford the opportunity to satisfy these criteria.

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A revolution in maize production

The agricultural outlook for 2005 depends on rainfall. The forecast of an El Nino effect indicates below-normal rainfall and higher-than-usual temperatures. This follows well below-normal winter rainfall in the Western Cape and low dam levels, with some areas already under water restrictions. In summer rainfall areas, rains came late and by end-November plantings had only been done in the eastern production areas.

However, some forecasters are relatively optimistic, pointing to the good yields last season despite below-normal rainfall in most areas.

Most prices - excepting vegetables - are not expected to increase much as they are already trading close to import parity, pulled down by the strong rand.

Crop estimates

The final maize crop estimate in October 2004 for the past season was 24% higher than the first estimate; the sorghum crop was 69% higher; and the soybean crop 48% higher. This resulted in the Crop Estimates Committee (CEC) being heavily criticised.

However, the conclusion of the debate was that grain production technology in SA has changed significantly over the past few years, increasing potential yields despite the adverse weather.

Factors that led to improved yields were a new generation of hardier cultivars; improved plant feeding technology where yields, fertiliser applications, etc, are planned with the help of satellite technology; better land preparation; a change in the application of chemicals due to GMOs (genetically modified organisms); a new generation of machinery; and less drought risk (especially with more land under irrigation at higher yields).

The result of these changes has been profound. Given the current 4.7m hectares under grain and oilseeds, indications are that crop sizes will continue to grow - especially maize, where a rising surplus above domestic needs will force prices down and enable SA's exports to compete with subsidised US exports.

However, given the problems with SA's transport and harbour infrastructure, costs are becoming prohibitive - apart from the lack of capacity to export 3m tons.

Calculations indicate that maize plantings, for example, should be reduced by at least 20% or 400,000-500,000ha to balance the market.

However, maize planting intentions for the new season indicate a 15.3% increase to 3.051m hectares, or a crop of 9-10m tons. This could give a stocks-to-usage ratio of 45%, against 35% in 2004.

Domestic prices were trading at close to import parity at end-November. Even in the worst case scenario of a severe drought, the potential for higher prices is limited. The continuous strength of the rand has pulled import parity considerably lower over the past year.

Sorghum planting intentions indicate the same area as last year - 118,000ha. The current crop of 360,000t is much larger than the domestic need.

Although the wheat crop is larger than last year's crop of 1.8m tons, imports of 900,000t will be needed. The planted area was raised by 14%, but drought in the Free State and Western Cape reduced yields to below break-even for producers. Prices dropped because of lower international prices and a stronger rand, leaving little room for price increases. Bread prices should now fall!

Oilseed planting intentions indicate a 9% decline; soybean planting intentions indicate an increase of 27%. Groundnut planting intentions are unchanged. SA will remain a net importer of oilseeds products, with local prices trading at import parity. Domestic price levels are falling in line with the fall in international prices due to record world crops.

Livestock

The supply of animals for slaughter increased substantially during the winter and early summer due to a lack of grazing. The decline in herd numbers will limit the supply of slaughter animals in 2005, while demand for meat remains relatively strong, driven by strong economic growth.

Domestic prices are at import price levels, though they are falling because of the strengthening rand. Import volumes are expected to grow in 2005, helping to restrain domestic prices.

In dairy, farmgate price levels have fallen, driven by the lower import prices and an increase in production (although this has not been reflected in retail prices).

The vegetable supply will be reduced this summer because a lack of irrigation water in production areas.

High temperatures will limit production. This could result in higher prices.

COMMODITY	LATEST PRICES (Brackets: 2-month ago prices)	YEAR-AGO PRICES	SHORT RUN PRICE TONE
White Maize (ex silo)	998 (977)	924	Sideways/lower
Yellow maize (ex silo)	988 (994)	981	Sideways/lower
Sorghum	908 (945)	1 037	Sideways/lower
Wheat (ex silo, Randfontein)	1 876 (1 448)	1 679	Sideways
Sunflowerseed (ex silo, Randfontein)	2 222 (2 129)	2 051	Lower
Soyabeans	1 852 (1 903)	2 564	Lower
Ground Nuts (Handpicked Quality)	4 000 (4 000)	5 000	Lower
Beef (Class A) (R/kg)	14.83 (14.28)	12.98	Sideways/lower
Lamb (Class A) (R/kg)	24.48 (23.37)	23.00	Sideways/lower
Pork (Porkers) (R/kg)	12.92 (11.82)	1.74	Sideways/lower
Broilers (Frozen) (R/kg)	10.39 (10.06)	10.36	Sideways/lower
Milk (Producer) (R/litre)	1.70 (1.70)	1.87	Sideways/lower
Potatoes (Class 1 Medium) (R/10kg bag)	18.60 (12.78)	23.03	Sideways/higher