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Lactose Processing Technology – Creating New Utilization Opportunities

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ABSTRACT

A significant contribution to displacement of fossil petroleum utilization can be made through the use of renewable waste and byproduct material for commodity chemical production. One such opportunity is lactose recovered from cheese whey. Several routes for use have been considered. A process involving catalytic hydrolysis of the lactose, catalytic hydrogenation to produce the sugar alcohols, and catalytic hydrogenolysis is proposed for production of mixed polyols as the product of choice.

Keywords: catalysis; hydrogenation; hydrogenolysis; hydrolysis; lactose; cheese whey

1. BACKGROUND

A new era in commodity chemical production is dawning. The green technology concept, which can be used to displace petrochemicals, is based on renewable feedstocks and waste minimization. Low-value leftover materials can be converted to marketable chemicals through newly developed catalytic and bioprocessing technologies.

In order to make these chemical products in an economically feasible manner, multi-step processes will be used following the model of modern petroleum refineries. Pretreatment and separation technologies will be key processing steps to facilitate this production. Combinations of biochemical and catalytic chemical processing will be used to maximize the efficiency of the processes. Effective recovery and purification of the final products will be crucial. In this paper, a process developed at Battelle, incorporating these steps, is applied to lactose recovered from cheese whey to produce high-value polyol chemicals.

Cheese processing has progressed through several levels of improvement relative to whey utilization. Whey has been the low-value byproduct from cheese manufacturing that for centuries on a small scale was usually recovered for its food value, but when extended to an industrial scale often was disposed as waste. With tighter restrictions forcing increases in waste utilization, whey was often placed into the animal feed market where practical. More recently, drying and recovery of the whey solids has become commonplace. As an extension of whey handling, further processing was considered and has become widely applied in the industry. Present efforts in whey protein recovery and refining are good examples of value-added byproduct utilization. The higher value protein led the way into the nutraceuticals market while the other major whey component, lactose, is now seeing wider recovery and utilization, primarily as a food component, but with new technology developments, its application and value could increase dramatically.

About 470 million pounds of lactose per year are the recovered from whey produced in the U.S cheese processing industry. Another 726 million pounds per year can come from European production. While the price of the lactose has varied from 10 to 30 cents per pound

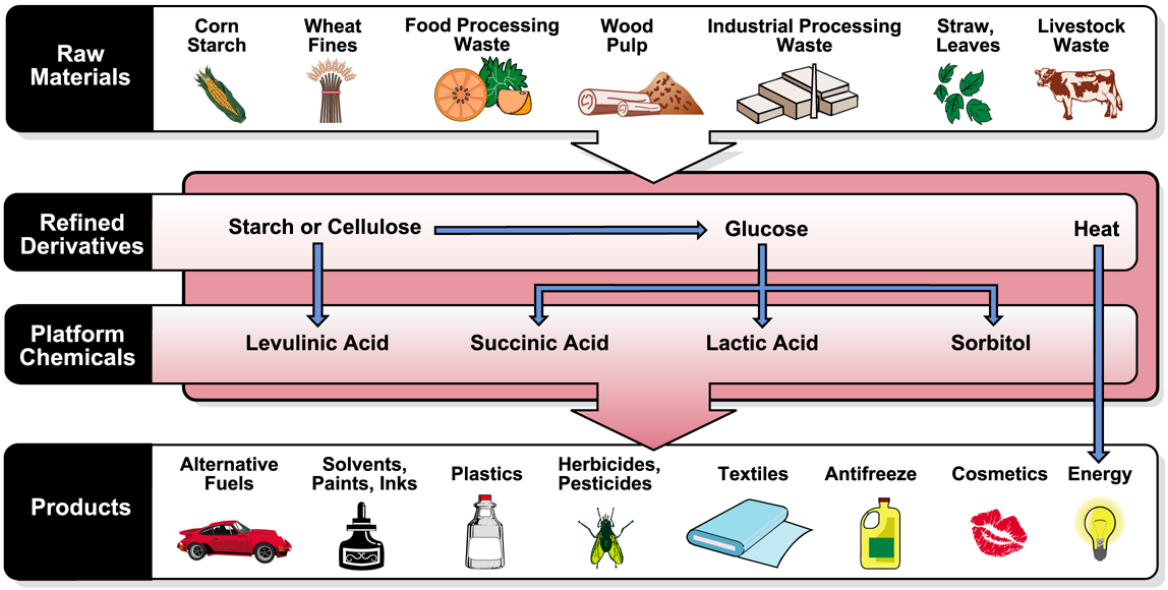
over recent decades, its current price is about 20 cents per pound. Further processing to chemicals can only be justified for products valued substantially higher. The process described here takes these economics into account and provides an option counter to a study completed nearly 15 years ago by the University of Wisconsin-Madison, which evaluated the potential of lactose conversion to a number of chemical products. That study concluded the market would not justify such production in competition with petroleum. However, it considered only fermentation products based on existing fermentation technologies (ethanol, acetic acid, butanol-acetone-ethanol, 2,3-butanediol, glycerol-ethanol, methane). It also made the comparisons at a time of particularly low petroleum prices (just after the price collapse of 1986).

Our proposed plan for utilization of lactose is based on value-added chemical product synthesis. As a carbohydrate resource, lactose has a highly oxygenated chemical structure, a disadvantage as a fuel because of its low energy density, but a distinct advantage as a starting material for the production of oxygenated chemical products. Its use eliminates the need for partial oxidation of the hydrocarbon structure found in petroleum. Such partial oxidations are difficult to control and typically inefficient on a carbon utilization basis due to byproduct (e.g., carbon dioxide) formation.

2. MULTI-STEP PROCESSING

A central concept for multi-step processes involves "platform" chemicals, which are produced in high yields as specific intermediates and serve as the basic building blocks for the final products. As illustrated in Figure 1, renewable feedstocks instead of fossil resources make up the raw materials. Figure 1 shows the relationships among some of the raw material feedstocks, refined derivatives, platform chemicals, and final consumer products. For the lactose utilization process described in this paper, cheese whey would be the food processing waste, and lactose would be the refined derivative that leads to glucose (and galactose) and sorbitol (and dulcitol). Further processing of the sugar alcohols yields polyol mixture, glycols and glycerol, which can be used in various products—from antifreeze to cosmetics to textiles.

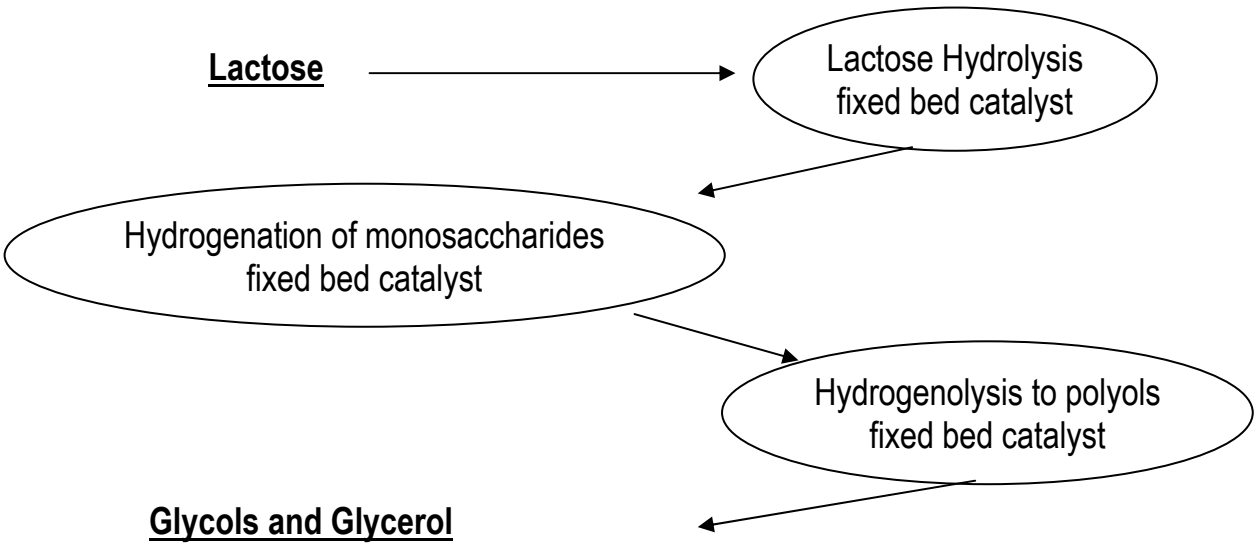
Figure 1. Overview of Processing Materials and Product Yields



3. LACTOSE UTILIZATION PROCESS

Our process for lactose utilization (patent pending, see Figure 2) involves three catalytic steps to break down and hydrogenate the lactose to produce polyol chemicals. All three catalytic steps are performed in an aqueous phase processing environment. In the first step, lactose, a disaccharide, is hydrolyzed to a mixture of monosaccharides, glucose, and galactose, by a solid acid catalyst. Next, the mixture of glucose and galactose is hydrogenated at low temperature by a ruthenium catalyst to a mixture of the sugar alcohols, sorbitol, and dulcitol. In the last step, the sugar alcohols are hydrogenolyzed in the presence of a base-activated metal catalyst to a mixture of polyols, primarily propylene glycol, ethylene glycol, and glycerol.

Figure 2. Battelle Process for Lactose Utilization



Although the lactose could be directly hydrogenated to a sugar alcohol (lactitol) as the first step, the advantage provided by the hydrolysis is the hydrogenolysis of the 6-carbon sugar alcohols instead of the 12-carbon sugar alcohol. By processing the 6-carbon feedstock, the possibilities for final product from the hydrogenolysis are simplified, leading to maximum yields of the desired 2- and 3-carbon polyol products. Hydrogenolysis of the 12-carbon sugar alcohol will result in a broad slate of polyol products potentially ranging from 2 to 11 carbons. Results to date have shown greatly reduced glycol yields (10%) when processing lactitol versus the 60-70% typically reported in the literature when processing sorbitol.

3.1 Product Potential

The glycol products are the same major organic chemicals now produced in the petrochemical industry. These chemicals are used in various well-known commodities, including antifreeze, food containers, and sugar substitutes. Annual U.S. production is at one billion pounds of propylene glycol and over six billion pounds of ethylene glycol. The propylene product is clearly the one of choice for production in the U.S. with a price around 68 cents per pound and a 4% growth in market size, while the ethylene product sells for only 28 cents per pound and has a growth rate of 3%. Both glycols are popularly known as antifreeze

components; ethylene is the common automobile radiator product, and propylene is the low toxicity substitute product, often used in potable water applications also. A larger market for ethylene glycol is in polyesters, such as the polyethylene terephthalate (PET) used for pop bottles and other food containers. The sorbitol (sugar substitute) market in food products is at about half a billion pounds annually, while the lactitol market is roughly estimated at less than one hundred thousand pounds.

3.2 Additional Products

Although the major products from the process are propylene glycol, ethylene glycol, and glycerol, there are also significant byproducts produced. These include butanediols and alcohols. Methane is also a significant product depending on the catalyst composition and condition.

4. TESTING AND RESULTS

Laboratory-scale batch-fed and continuous-flow reactor studies were conducted to demonstrate the ability of lactose processing to produce value-added chemical products. Acid hydrolysis and enzymatic hydrolysis tests were performed on lactose and whey permeate. We have extensive experience (both batch-fed and continuous-flow) in the catalytic hydrogenation of glucose, as well as some work with lactose, galactose, and whey permeate. The hydrogenolysis of sorbitol and lactitol was also studied.

4.1 Hydrolysis

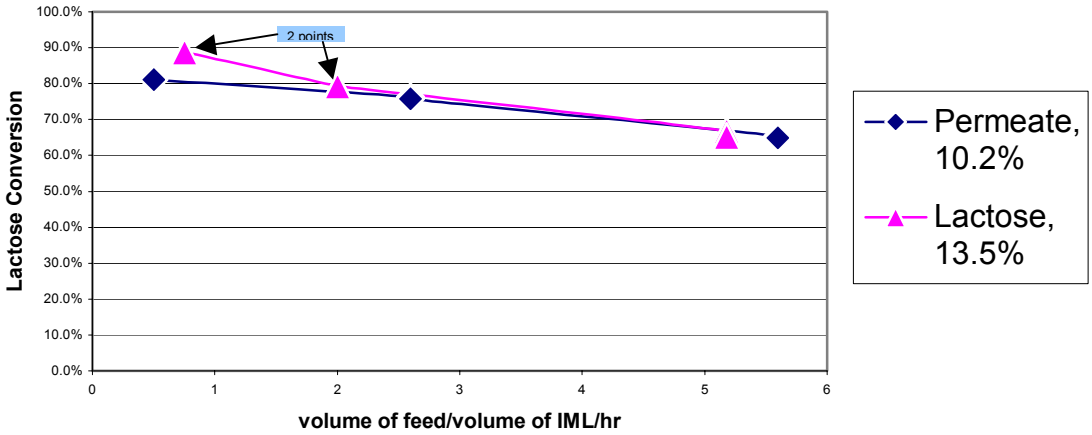
Lactose hydrolysis can readily be accomplished either with a mineral acid system or with enzymes. Typically, the process is performed batch wise, with the addition of free acid or enzyme to the solution. In a large-scale application for industrial production, the use of solid acid or immobilized enzyme provides several advantages. In both cases, the catalyst is maintained in the reactor system and not lost into the product, providing a savings in the cost of the solid catalyst. Further, without incorporating the catalyst into the product solution, the product post-treatment costs should also be reduced. Finally, the acid catalyst or enzyme added in the first step could poison the catalysts used in the second and third steps if they are allowed to pass on freely with the hydrolyzate product.

Our studies included both the free enzyme and the immobilized enzyme in lactose hydrolysis. The enzyme, beta-galactosidase, can be produced in either of two forms, a yeast-derived form that operates in a neutral environment or a fungal product that is acid tolerant (actually requires an acid environment).

4.1.1 *Hydrolysis with immobilized enzyme:*

A fixed bed of immobilized enzyme (IML) from Valio Engineering, Ltd., Helsinki, Finland, was used for the hydrolysis of lactose and cheese whey permeate concentrate. The immobilized enzyme came from a GRAS organism on a food-grade adsorption resin. The fungal-derived enzyme was rinsed free of the acetic/sorbate storage medium, and the feedstock pH was measured at 4.9. The lactose feedstock was essentially a saturated solution of refined lactose at room temperature, and the permeate solution was processed as received. The tests were performed in a small tubular reactor at room temperature. Processing results are shown in Figure 3. Further optimization of the processing conditions is needed to achieve the high level of hydrolysis (near 100%) expected for our process.

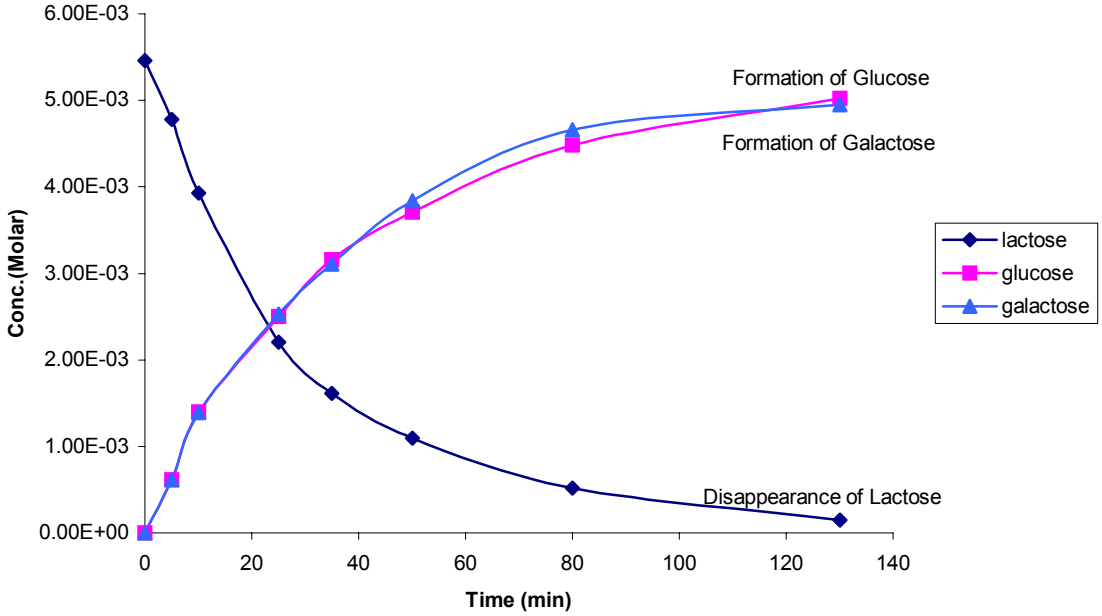
Figure 3. Lactose Conversion as a Function of Processing Rate Valio Immobilized Enzyme @ 21C



4.1.2 *Hydrolysis with acid:*

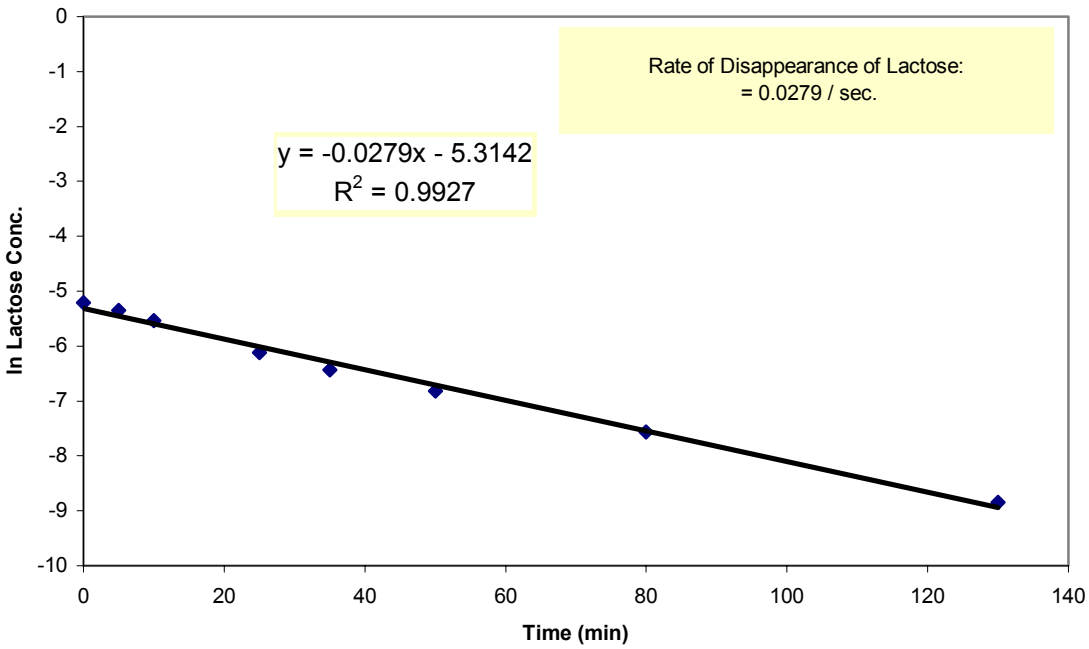
Acid catalysts for lactose hydrolysis can also be used in either of two forms: 1) free acid, such as sulfuric acid, can be added to the solution or 2) a solid acid, such as the acid form of a cationic exchange resin, can be used to treat the lactose solution. We used the free acid hydrolysis of lactose for these tests. The hydrolysis tests were performed in small, sealed glass ampoules heated in a sand bath, and the products were analyzed with liquid chromatography. Figures 4 and 5 show the ready hydrolysis of the lactose and the excellent selectivity to the two

Figure 4. Lactose Conversion at 120 C and 0.2 wt% conc. H_2SO_4



monosaccharide portions of the lactose, glucose and galactose. No other byproducts were noted. A kinetic analysis of the data suggests that lactose hydrolysis proceeds more readily than cellobiose (another C_6 disaccharide sugar) but less readily than xylobiose (a C_5 disaccharide sugar).

Figure 5. Lactose Concentration vs. Time



The use of the solid acid allows for continuous-flow processing without contaminating the products with the free acid. In process applications, we intend to use Applexion XA 969 H resin specifically designed for disaccharide hydrolysis. With this resin high conversion of the disaccharide to monosaccharides can be achieved with minimal formation of oligosaccharides, which is a complication found in the enzymatic process[i].

4.2 Hydrogenation

Catalytic hydrogenation of saccharides (aldoses) to sugar alcohols (alditols) is well known and even commercially practiced for certain cases. Glucose to sorbitol is a large-scale component of the food processing industry (as described above). Maltitol is also produced from maltose, and lactitol is produced from lactose, but both on a much smaller scale. The bulk of these processes are operated as batch hydrogenations using nickel metal catalyst.

Our work over the years with aqueous phase catalytic hydrogenations has shown that new, more stable, catalyst formulations are required for aqueous phase processing. Consequently, we have moved from the silica and alumina supports typically used (and inherited from petroleum processing) to titania or carbon supports. These materials are less susceptible to dissolution or hydrolysis in the water environment used here. Further, we have developed stabilized nickel catalysts[ii] and tested the use of ruthenium[iii] for these hydrogenations. The

ruthenium catalysts are more active than nickel, requiring a much lower metal content, and are more stable, causing much less contamination of the product solutions.

Batch reactor protocols developed in our studies were used for the comparative assessment of catalysts and processing conditions. A combined Parr bomb (300 mL) with stirrer and a high pressure sampling system were employed to produce data for kinetic models. This equipment configuration was also used to evaluate chemical mechanisms through analysis of chemical intermediates and products as a function of time at processing conditions.

As an extension, laboratory-scale continuous-flow reactor systems were used for evaluating the catalysts in a fixed-bed configuration in a tubular reactor. In these systems, the feedstock solution is pumped continuously by a twin-piston metering syringe pump into the top of the tubular reactor where it mixes with an incoming stream of metered hydrogen gas. The gas and liquid phases pass down through the catalyst bed, which is maintained at temperature (100°C) by hot oil flowing around the reactor tube from a closed-system, circulating oil bath. Pressure (1200 psig) in the reactor is maintained by a back-pressure regulator. Once the products pass out of the back-pressure regulator, they are cooled, the liquids collected, and the gases metered and sampled for subsequent gas chromatography analysis. Representative results are given in Table 1.

Table 1. Sugar Hydrogenations in a Fixed-Bed, Continuous-Flow Reactor (1900 psig)

Feedstock	Temp. deg C	LHSV	wt% Feed concentration	feedstock conversion	alditol yield, %	gas yield, % carbon basis
Lactose	100	2	18.4	100	95	0.06
	100	3	18.4	99.7	96	0.05
	100	4	18.4	99.2	98	0.05
Xylose	100	4	19.6	100	99	0.17
Glucose	100	4	19.9	100	96.7	0.16
	100	6	19.9	99.95	99.8	0.14
	100	2	39.8	99.98	95.5	0.21
	100	4	39.8	98.55	95.3	0.2

4.3 Hydrogenolysis

While widely reported in the chemical literature[iv] for over 40 years (and even reported as early as 1933[v]), hydrogenolysis has yet to be practiced commercially on any of the potential feedstocks. Our early work focused on the catalyst and optimization of conditions to favor one or the other of the glycol or glycerol products[vi]. The process is accomplished in the same configuration as the hydrogenation, except at more severe conditions (200°C and 2000 psig). The choice of processing conditions and catalyst can greatly affect the composition of the product mix. Recovering the products in sufficient purity is a key issue in the commercialization of the technology.

The complexity of the product slate has a major effect on the final product purity. Herein lies an advantage for the preliminary hydrolysis of the lactose prior to hydrogenation. The product slate from hydrogenolysis of the C_{12}, lactitol, is much more complex than the product slate from a mixture of C_6s, sorbitol and dulcitol, which each produce the same products. While the lactitol hydrogenolysis could lead to a number of interesting polyol ether products, the potential number of products is greatly increased and thus the purification problem is greatly

magnified. We have chosen the use of the hydrolysis step prior to hydrogenations and hydrogenolysis in order to simplify the product slate and resulting recovery steps.

6. FUTURE PLANS

Lactose is currently recovered and purified in several cheese processing facilities. Use of this refined lactose product as a chemical feedstock can be accomplished using the three-step process we have envisioned for hydrolysis, hydrogenation, and hydrogenolysis of the lactose to produce polyols, i.e., propylene glycol, ethylene glycol and glycerol. Laboratory scale tests have demonstrated the technical feasibility of the process steps. The combination of the three steps can be reasonably accomplished if a solid acid catalyst or immobilized enzyme is used in the initial hydrolysis step to eliminate the need for addition of free acid, which could contaminate the catalyst used in the subsequent hydrogenation/hydrogenolysis steps.

Today's chemical and fuel industries are based primarily on fossil fuels, but the use of cheese whey lactose streams is a first step leading to a full-scale biomass to chemicals industry. Over the next two decades, this type of technology has the potential to transform major sectors of the chemical and fuel manufacturing industries in the U.S. and abroad from petroleum-based to renewable feedstock.

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