NREL Advances in Research at the National Renewable Energy Laboratory

Research Brief

# Continual Shrinking-Bed Reactor Boosts Biomass Ethanol

## NREL Researchers Dramatically Improve Pretreatment Process

Old-time moonshiners were known for making ethanol for drinking from "corn squeezins." Now, modern- day scientists are making ethanol for the automotive fuel of the future by "squeezin" or shrinking their pretreatment reactors. Their continual shrinking-bed reactors, together with two other innovations for the first stage of the process for producing ethanol from biomass, could dramatically improve the economics of this promising technology for replacing imported oil with home-grown fuel.

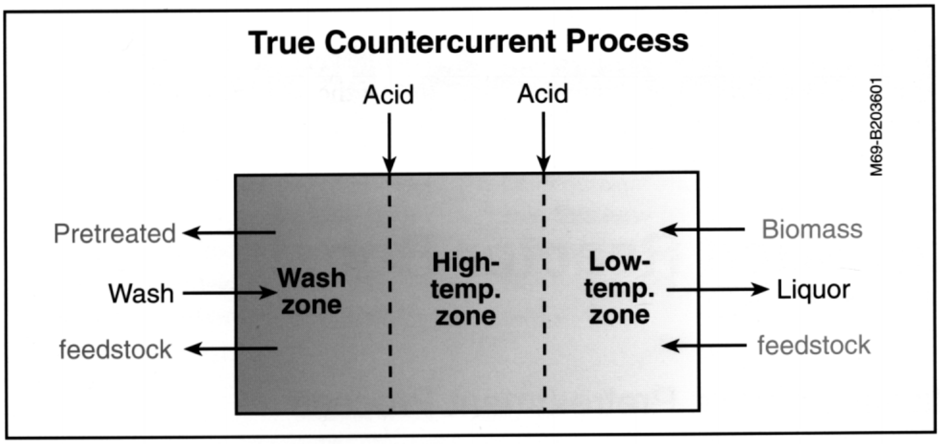
The National Renewable Energy Laboratory (NREL) is a leader in developing technology to make ethanol from cellulosic materials such as trees or grasses or waste materials. The moonshiners had it pretty easy: a common enzyme breaks down starch such as corn into sugar, and common yeasts readily ferment that sugar to ethanol. But when we are making ethanol from nonfood biomass, the cellulose and hemicellulose are much more difficult to break down into their component sugars. The main steps in a process that will accomplish this may include (1) thermochemical pretreatment to hydrolyze the hemicellulose (break it down to sugars) and expose the cellulose for subsequent processing, (2) enzymatic hydrolysis of the cellulose to break it down to sugars, and (3) separation or joint microorganism fermentation of the cellulose and hemicellulose sugars to ethanol.


Warren Gretz, NREL/PIX04155

This laboratory-scale apparatus simulates countercurrent movement of liquid and solids in a series of continual shrinking-bed reactors. The reactors, which are shown lifted out of their hot-sand baths, have springs that shrink the reactor volume as biomass carbohydrates hydrolyze and the sugars (now liquid) flow out.

NREL researchers have recently developed three pretreatment innovations that could reshape biomass-to-ethanol technology. Two-temperature processing takes advantage of the fact that one portion of the hemicellulose hydrolyzes more easily than the other. Countercurrent processing quickly removes the product sugars from the reactor so that they are not degraded. Shrinking the reactor bed as the process progresses reduces the amount of dilute acid that must be heated and results in higher sugar concentrations. Using the first two of these innovations greatly improves the pretreatment process itself: the direct yield of sugar from hemicellulose is significantly higher, the cellulose can be enzymatically hydrolyzed in less than half the time, and the acid used need not be nearly as strong.

Adding the shrinking-bed-reactor feature makes it feasible to also add a third, higher-temperature stage and hydrolyze much of the cellulose as well. This opens the door to being able to substantially reduce or even eliminate the need to produce cellulase enzymes for cellulose hydrolysis. Cellulase enzyme




This conceptual representation of a dilute-acid, two-temperature countercurrent pretreatment process shows how hydrolyzed sugars (liquor) are removed from the reactor before being subjected to conditions harsher than necessary to hydrolyze them.

production is currently a costly element of biomass-to-ethanol technology. In some designs it also consumes cellulose that would otherwise be available for ethanol production. NREL is pursuing improved pretreatment processes in conjunction with efforts to develop advanced cellulase production technology to improve the economics of biomass ethanol production.

## Dilute Sulfuric Acid Plus Heat Make an Effective Starting Point

The first step in pretreating lignocellulosic material is to chip, mill, or grind biomass to make it more accessible to chemical treatment. Next, in the presence of a chemical catalyst, the material is subjected to high temperature to alter the lignin-hemicellulose sheath. NREL has focused most of its in-house research and development in pretreatment on the use of dilute sulfuric acid at elevated temperature and pressure. Advantages of dilute-sulfuric-acid pretreatment over many other pretreatment processes include a high yield of sugars from hemicellulose, low catalyst costs, and easier neutralization.

The sulfuric acid treatment hydrolyzes hemicellulose to xylose and other sugars that dissolve in the water media. Most of the cellulose remains solid with the lignin, but it is now more accessible because the lignin-hemicellulose sheath has become porous as a result of the removal of hemicellulose. The cellulose can now be effectively converted to sugar by cellulase enzymes, and the lignin may be used as boiler fuel to provide heat and electricity for the production process. In cooperation with Oak Ridge National Laboratory, NREL has examined a large number of herbaceous and hardwood feedstocks and found that the dilute sulfuric acid works well for all of them. Researchers are now also exploring use of this pretreatment process for softwoods, such as those from logging residue.

## Countercurrent Prevents Degradation, Allows Lower Acid Level

The biggest problem with dilute-acid pretreatment occurs after the hemicellulose has hydrolyzed to xylose and other five-carbon sugars.

The high temperature of the acid solution tends to degrade the xylose. To limit xylose degradation, NREL researchers are applying a countercurrent system in which the biomass

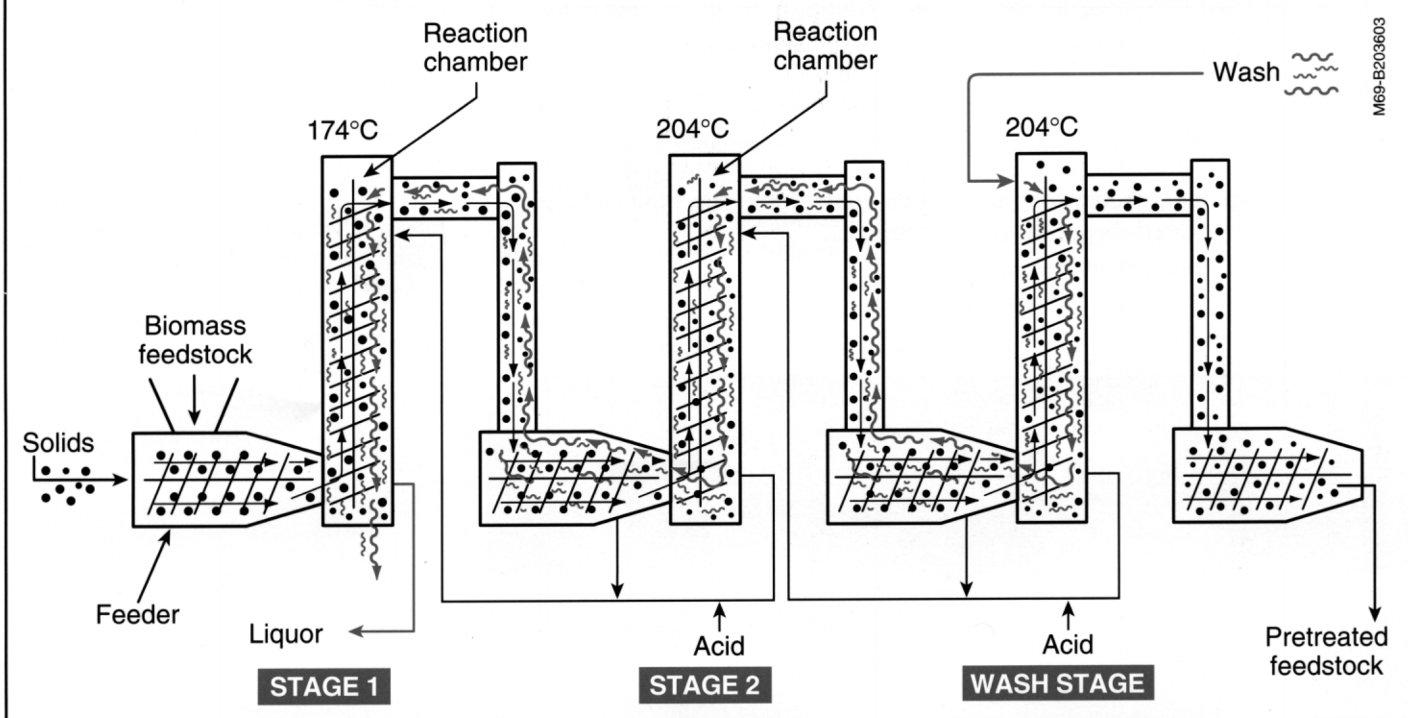
## Why Pretreatment?

Someday you may fill your car's fuel tank with a high-octane, clean-burning domestic fuel made from corn cobs and stalks, forestry scrap, and even municipal solid waste or specially grown energy crops such as fast-growing trees or grasses. Cellulosic biomass materials such as these are environmentally friendly energy sources whose use could mitigate trade balance problems, dependence on foreign oil, and contributions to global climate change, while eliminating waste problems and promoting new domestic industries. NREL is leading efforts to develop biomass-to-ethanol technology to tap this potential energy.

The problem is that this energy is "locked up." Sugars and starches—the carbohydrates that people can digest and that most yeasts can ferment—have relatively accessible structures. Sugars are single molecules and starches are chains of sugar molecules with linkages that can be broken by common enzymes. Sugar and starch, however, are generally too expensive to use in making low-cost fuel. But cellulose and hemicellulose, the carbohydrates in inexpensive woody and fibrous plant materials, are long chains of sugar molecules with more resistant linkages; cellulose also has hydrogen bonds between chains that form a crystalline structure.

Researchers have developed ways to produce enzymes that break down or hydrolyze the bonds between the sugar molecules in cellulose, but the cellulose is protected from enzymatic attack by a sheath of hemicellulose and lignin. The challenge of pretreatment is to disrupt this sheath and release the alcohol fuel potential of the cellulose without destroying the sugars in the hemicellulose.

## Conceptual Design of Countercurrent Flow, Two-Temperature Pretreatment Process




This schematic representation of a two-stage, countercurrent pretreatment process using vertical screw reactors shows how a large-scale system might be configured.

feedstock is fed in at one end and the hot acid solution at the other. As the hemicellulose sugars hydrolyze and dissolve, they flow back out the end into which the solid feedstock is being fed. This removes them from exposure to high temperatures relatively soon after they hydrolyze, thus reducing degradation. This substantially reduces the sugar-degradation potential associated with batch processing, in which liquid sugars must remain in the vessel until nearly all of the hemicellulose hydrolyzes.

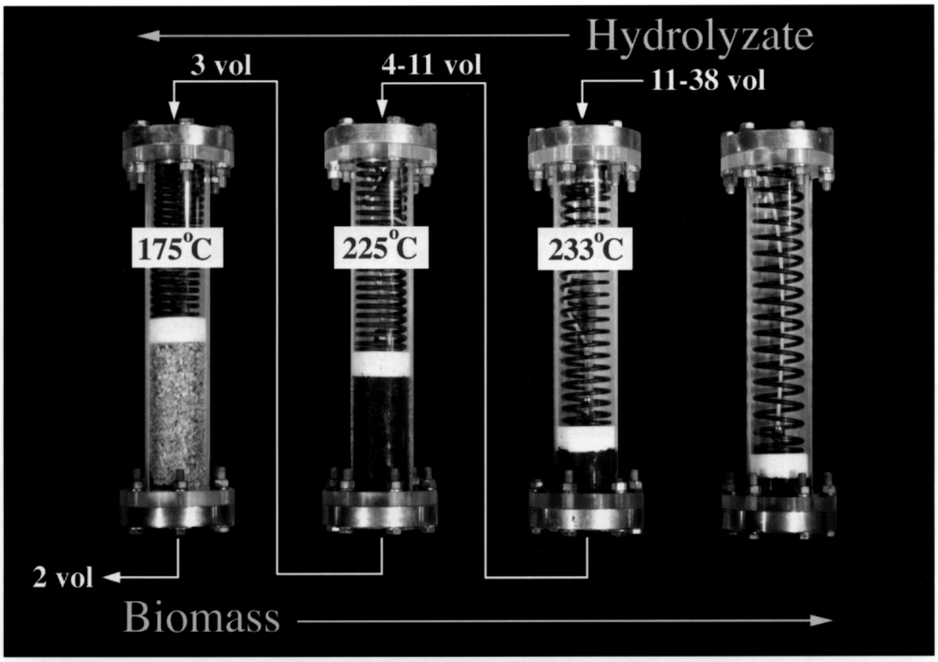
A key benefit of removing the hydrolyzed sugars from the reactor soon after formation is that higher temperatures can be used because there is less concern about degrading the sugars. This in turn allows the acid to be even more dilute, because temperature and acid concentration can be traded off for each other to achieve effective pretreatment. By increasing temperatures 15°C to 45°C higher than the approximately 160°C used for batch pretreatment, NREL researchers have been able to reduce the sulfuric acid concentration to one-tenth of what was previously needed.

### Two-Temperature Processing Increases Yield

Another pretreatment innovation by NREL researchers originated from the observation that hemicellulose was being released from hardwoods and many other biomass feedstocks in two fractions, one relatively easy to hydrolyze and the other more difficult. To take advantage of this, and simultaneously apply the countercurrent concept, NREL researchers designed a process that first subjects the biomass to a relatively low temperature (174°C).

With the countercurrent design, this allows the easy fraction to hydrolyze and those liquefied hemicellulose sugars to be removed. The remaining biomass moves on to a second, higher-temperature (204°C) chamber in which the harder fraction of the hemicellulose hydrolyzes. The sugars released flow back to the first chamber, in which degradation is minimized by the lower temperature. The pretreated biomass (minus hemicellulose) is washed with hot water (in the same or a third chamber) to rinse out the acid, preparing the remaining cellulose for enzymatic hydrolysis.

NREL has obtained excellent results with countercurrent, two-temperature pretreatment combining these two innovations. Pretreatment now recovers more than 95% of the sugars from hemicellulose, an increase in yield of 10% to 15% over single-stage batch processing. Nearly all of the hemicellulose and about half of the lignin are removed by the pretreatment. This—probably particularly the lignin removal—allows the remaining cellulose to be more easily



With a three-stage temperature design such as this, countercurrent, shrinking-bed reactors would hydrolyze cellulosic as well as hemicellulosic carbohydrates, becoming a total hydrolysis rather than a pretreatment system.

digested in subsequent enzymatic hydrolysis. Fermentation of biomass pretreated with the new process produced 91% of the theoretical yield of ethanol in 2.5 days compared with only 70% to 85% after 6–7 days following conventional batch pretreatment (using simultaneous saccharification and fermentation of pretreated yellow poplar sawdust).

## Shrinking-Bed Reactor Reopens Door to Cellulose Hydrolysis

As NREL researchers were developing the use of countercurrent, two-temperature pretreatment they realized that the new process was capable of thermochemically hydrolyzing a significant amount of the cellulose. This led them to seriously investigate thermochemical processing for cellulose hydrolysis as a way to reduce the cost of biomass-to-ethanol technology as a whole.

When NREL researchers seriously investigated full thermochemical hydrolysis—including cellulose—about 10 years ago, they concluded that it was possible to get good yields of glucose from cellulose thermochemically, but that the problems associated with using stronger acid or higher temperature were too great. The former would require an effective way to recover the acid, and the latter necessitated very short residence times so the glucose would not be degraded by the high temperatures. The heated acid solution had to be pumped through very quickly, so a large volume would be required. The expense of heating, cooling, and then treating this large amount of solution appeared prohibitive, so NREL chose to focus on enzymatic hydrolysis of cellulose using thermochemical action as a pretreatment to make the hydrolysis easier.

Countercurrent processing shortens residence time and two-temperature processing avoids exposure to very high temperatures for some of the sugars produced—and thus both reduce degradation concerns. Researchers now had a big step up on avoiding the need to flush large volumes of solution through the reactors. The major breakthrough, however, came when the researchers realized it would be possible to reduce the pretreatment reactor size—and therefore the liquid requirement—correspondingly with the reduction in solid material as hydrolysis proceeds. In the initial laboratory system, NREL's shrinking-bed reactor uses spring-loaded plungers to continuously reduce reactor size for each stage of the pretreatment process. But to convert the concept to a commercial-scale design, researchers will be looking at continuous screw drives, pistons, and other mechanical systems.

The reduced volume of acid solution made possible by adding a shrinking-bed reactor to countercurrent processing makes thermochemical hydrolysis of cellulose, which had to be abandoned 10 years ago, look very attractive now. By increasing the temperature of the second stage of their two-temperature system from 205°C to 225°C, NREL scientists found that they could successfully hydrolyze about half of the cellulose along with the harder fraction of the hemicellulose. To hydrolyze the rest of the cellulose, they are now analyzing whether it would be better to hold the material longer in this second reactor or to add an additional third reactor at 235°C. NREL analysts will also be determining whether the economics are better for a two-temperature thermochemical pretreatment process that reduces the amount of enzymatic cellulose hydrolysis needed or for a two- or three-temperature process that fully hydrolyzes the cellulose.

## Potential is Great to Improve Economic Effectiveness

Approximately one-third of the carbohydrate potential of lignocellulosic material comes from hemicellulose, and two-thirds, from cellulose. Increasing the sugar yield from hemicellulose by 10% to 15%

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with multistage, countercurrent pretreatment should therefore result in a direct increase of 3% to 5% in total ethanol production. Similarly, facilitating enzymatic hydrolysis increases the fermentation yield from cellulose 6% to 21% beyond that of batch pretreatment. This produces a 4% to 14% increase in yield, for an overall total improvement from both cellulose and hemicellulose of 7% to 19%. The dramatic yield increase achieved at the bench scale with multistage, countercurrent pretreatment alone could make a major difference in the economic competitiveness of biomass-to-ethanol technology.

Researchers will now quantify the yield improvement obtained in an integrated, engineering-scale process to determine commercial feasibility. The new pretreatment process requires reactors that are more complex and operate at higher temperature and pressure. However, the cost of heating the water and acid solution to higher temperatures may be the biggest economic challenge. There are also somewhat larger volumes of liquid. But the shrinking-bed-reactor design reduces considerably the volume of heated solution needed.

NREL researchers are now focusing on the economics of the new pretreatment techniques to optimize their cost-effectiveness (instead of just yield). NREL will use the results of these analyses in designing pretreatment processes as they scale up the demonstration of ethanol production from laboratory to pilot plant.

## But Some Challenges Must Still be Met

NREL is now applying industrial expertise to overcome technical hurdles to turning its new pretreatment technology into a viable commercial process. The most basic obstacle is scaling the process up to production levels. The new pretreatment process has been carried out in 5-cm (2-in.) diameter reactors, but the next stage will use 15-cm (6-in.) diameter reactors. At this pilot scale, researchers expect to be able to use the same types of devices that would be used for industrial production.

In moving to this pilot scale, NREL scientists would also like to move to a true countercurrent process in a single reactor instead of using separate chambers, as they do now. Both of these changes will create challenges in the mechanics of moving small particles of biomass through the system, against the liquid flow, while getting the solids and liquids to mix well. The flow mechanics of the system become particularly challenging if carried through to complete cellulose hydrolysis. With all the hemicellulose and cellulose gone, the last reactor is left with a very dense mass of mostly lignin. Current biomass technology contemplates using the lignin as a fuel, but its greatest value may be as a chemical for making various coproducts. One possible use is for making adhesives, which indicates how difficult it may be to work with lignin in a reactor.

Although some of the lignin remains solid after the new pretreatment process, an entire area of new challenges is posed by countercurrent pretreatment, because the new process also hydrolyzes a substantial amount of the lignin—about 40% in a two-temperature process and 60% in a three-stage process including cellulose hydrolysis. (Lignin probably also hydrolyzes in batch pretreatment but then reprecipitates as the batch cools.) Removing lignin may be a major factor in enhancing cellulose hydrolysis and fermentation, but it also produces various toxic or inhibitory substances whose impact needs to be minimized. A key part of future NREL research will be to develop mechanisms to detoxify and separate out the hydrolyzed lignin to prevent interference with hydrolysis and fermentation of the cellulosic and hemicellulosic sugars.

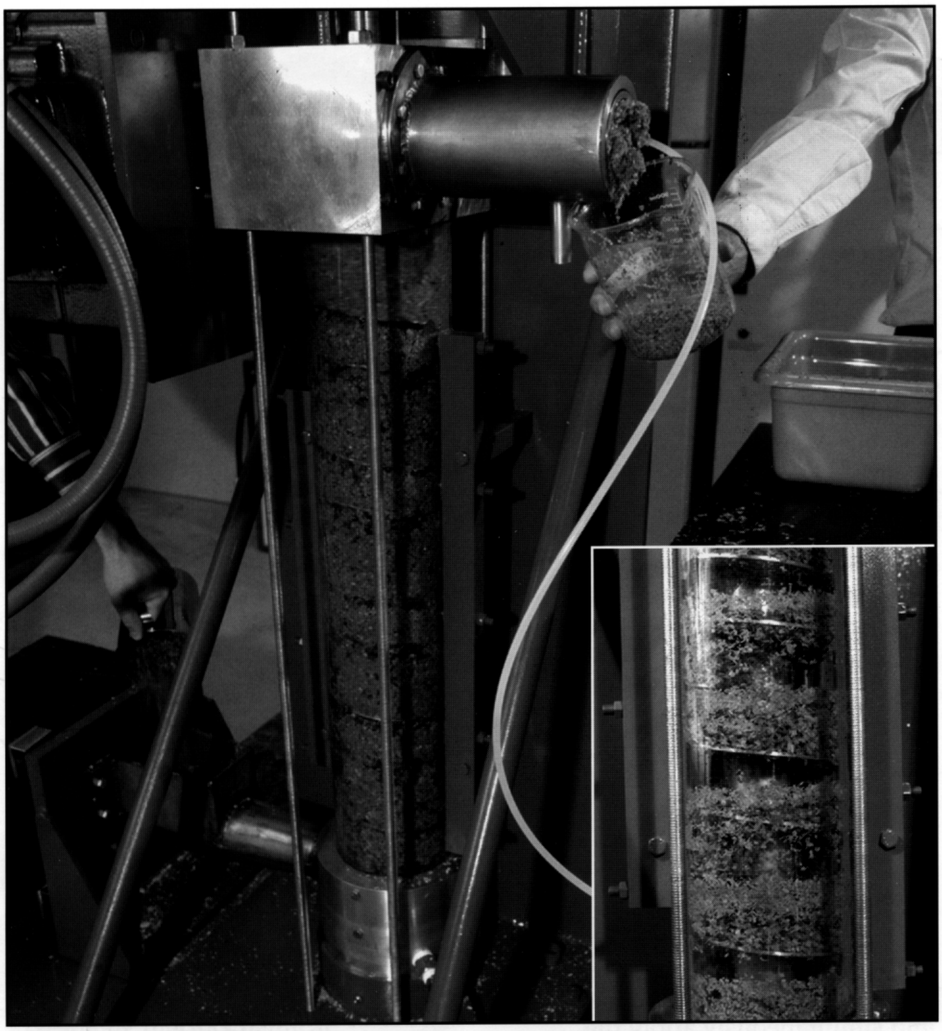
It is also economically important to recover the hydrolyzed lignin. The solid lignin that makes it through the fermentation process with conventional batch pretreatment is a valuable resource for use as boiler

### Alternate Technologies

Although NREL's direct pretreatment work has focused upon dilute sulfuric acid, the Laboratory also supports the development of other options by other research groups. The goal is to develop technology for producing ethanol at the lowest possible cost for a wide range of feedstocks. Six two-year subcontracts issued in 1993 to university and industry researchers have been completed. Two of them investigated using different acids for pretreatment, two investigated different alkalis, one examined ammonia freeze explosion, and one explored hydrogen peroxide extrusion. Analysts are now sketching out the kinds of industrial processes that would be required for these techniques to determine their economic potential.

fuel. A recovery process for liquefied lignin from countercurrent pretreatment should yield either a solid for fuel or a valuable chemical feedstock.

NREL researchers are eager to meet these challenges and develop their countercurrent, multitemperature, shrinking-bed-reactor pretreatment process into an industrial countercurrent pretreatment system. The potential improvement in the economics of the full biomass-to-ethanol technology is tremendous. And they know how important an economic and environmental role this new technology could play in creating a new industry producing fuel from lignocellulosic material.



Warren Gretz, NREL/PIX01638 and 01598

NREL researchers are using this prototype vertical screw reactor to determine mass transfer and residence time characteristics in preparation for scale-up to an industrial system.

## Patents and Publications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Produced by the Communications Center for the Center for Renewable Fuels and Biotechnology
NREL/BR-420-21221 4/97

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