Hydrogen from Biomass by Autothermal Reforming

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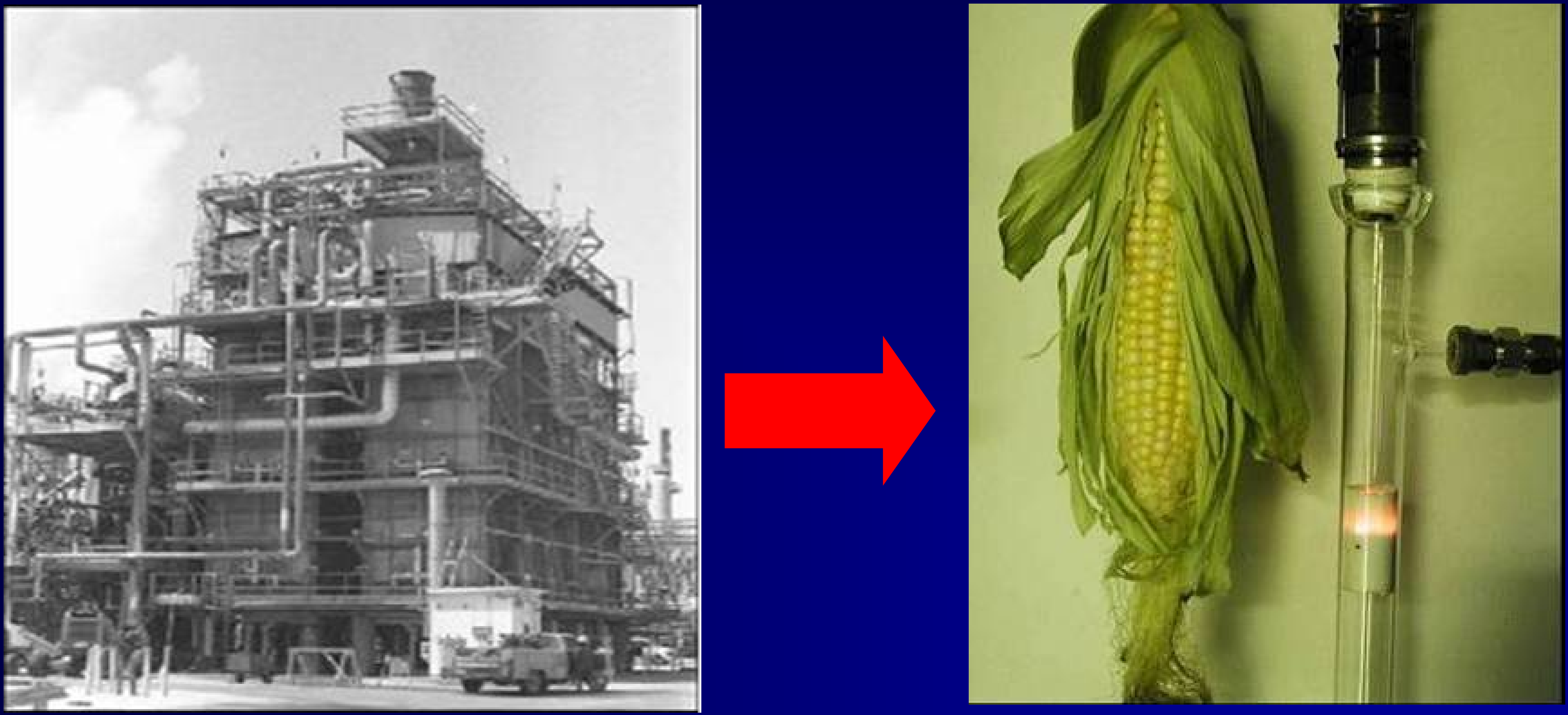
Fuels Reformed by Catalytic Partial Oxidation

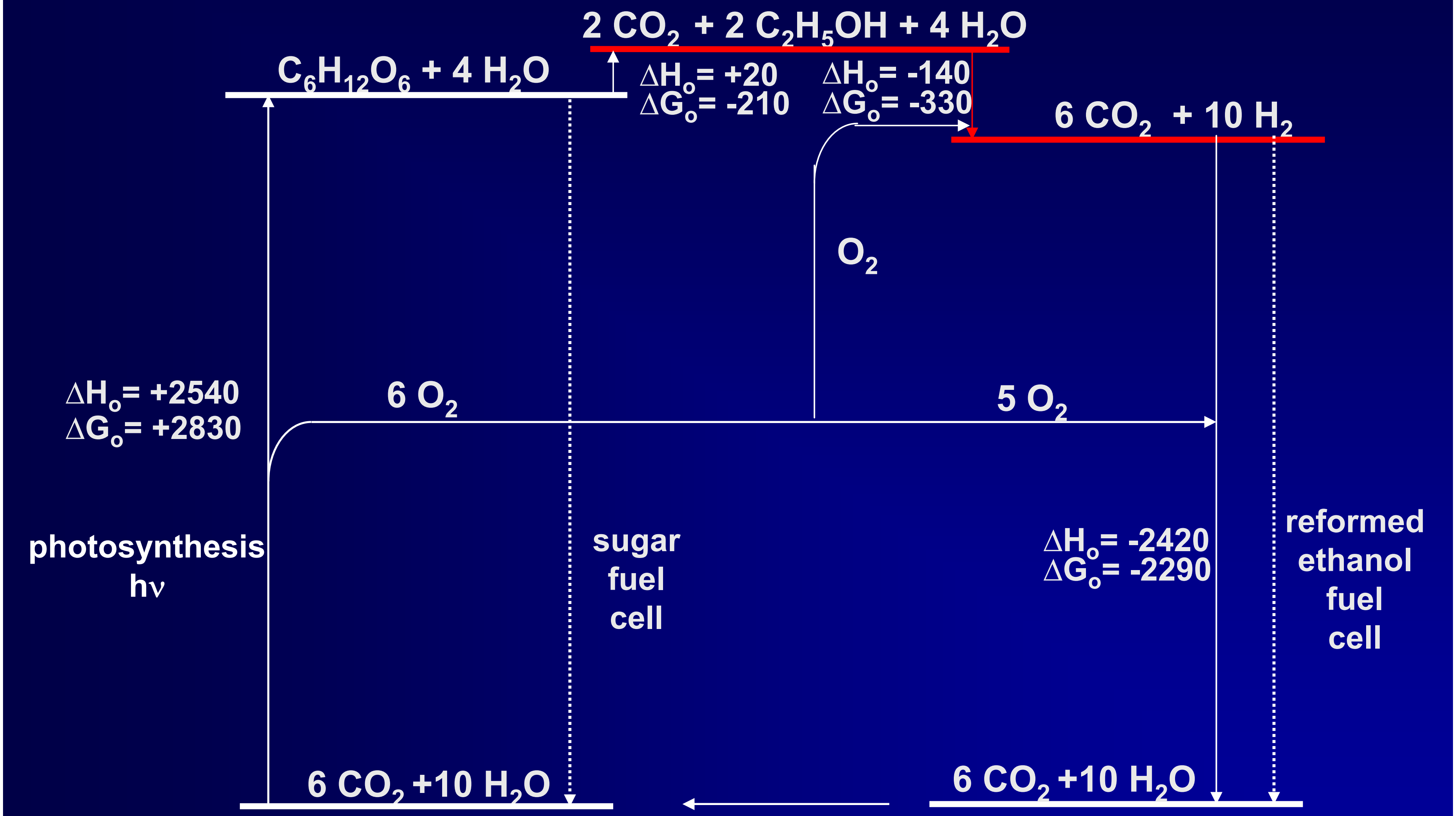
methane
ethane
propane
butane
hexane
octane
*decane
hexadecane
toluene
naphthalene
diesel
JP-8

ethanol
methanol
propanol
ethylene glycol
glycerol
biodiesel
soy oil
glucose-water

At least 20 hours with <1% deterioration
1 to 10 millisecond residence times
>80% H_2 and CO selectivities



Energy Diagram for Ethanol



$2\ CO_2 + 2\ C_2H_5OH + 4\ H_2O$

$C_6H_{12}O_6 + 4\ H_2O$

$\Delta H_o = +20$
$\Delta G_o = -210$

$\Delta H_o = -140$
$\Delta G_o = -330$

$6\ CO_2 + 10\ H_2$

O_2

$\Delta H_o = +2540$
$\Delta G_o = +2830$

$6\ O_2$

$5\ O_2$

photosynthesis
hν

sugar
fuel
cell

$\Delta H_o = -2420$
$\Delta G_o = -2290$

reformed
ethanol
fuel
cell

$6\ CO_2 + 10\ H_2O$

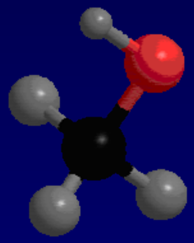
$6\ CO_2 + 10\ H_2O$

Carbohydrates

Methanol

Boiling Point = 65 ^{o}C

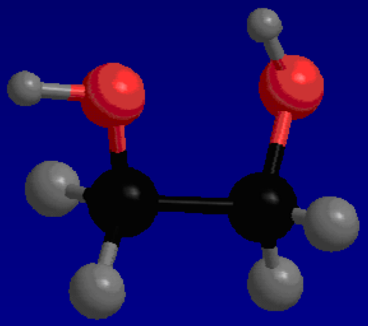
$H\text{-}(CH_2O)\text{-}H$



Ethylene Glycol

Boiling Point = 195 ^{o}C

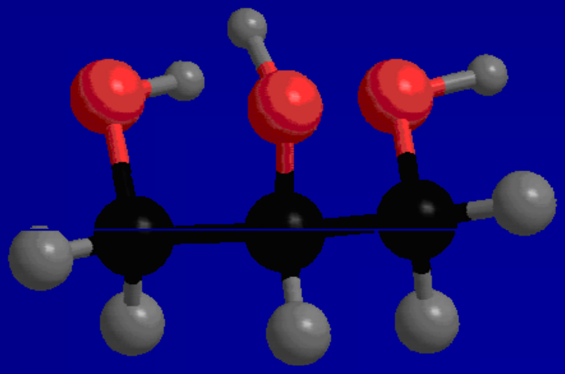
$H\text{-}(CH_2O)_2\text{-}H$



Glycerol

Boiling Point = 290 ^{o}C

$H\text{-}(CH_2O)_3\text{-}H$



Mechanism

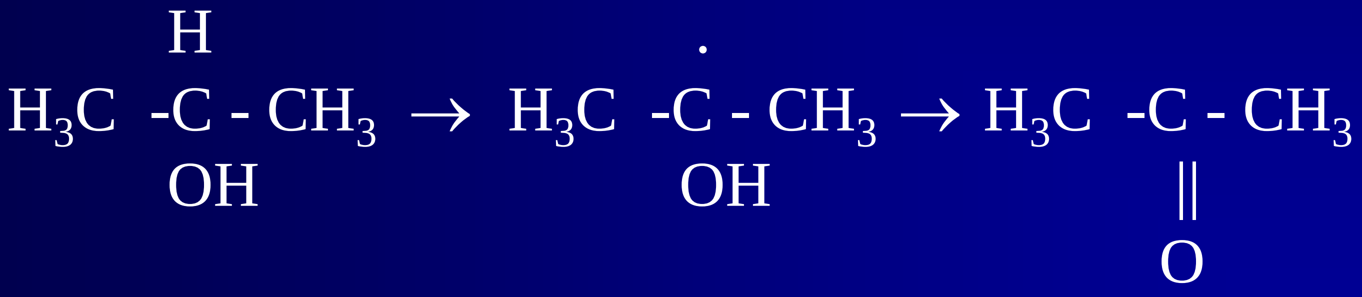
Surface

$ROH \rightarrow RO(s) \rightarrow H_2 + CO$

surface alkoxy makes syngas

only C_1 species

Homogeneous



$$H_3C-\overset{H}{\underset{OH}{C}}-CH_3 \rightarrow H_3C-\overset{\cdot}{\underset{OH}{C}}-CH_3 \rightarrow H_3C-\underset{\underset{O}{\|}}{C}-CH_3$$

chemistry very selective

no secondary products

Renewable Hydrogen from Nonvolatile Liquids by Reactive Flash Volatilization

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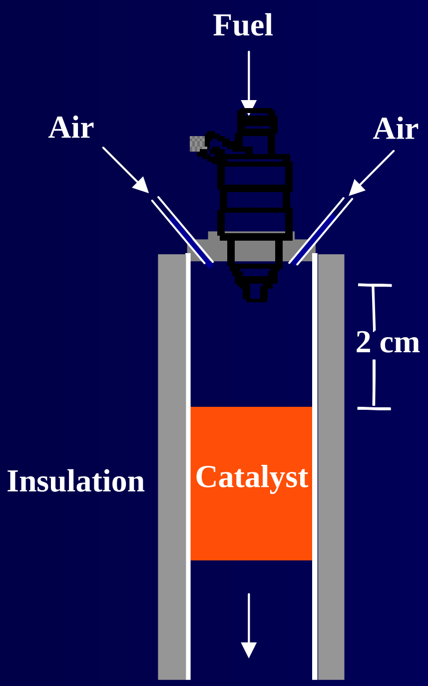
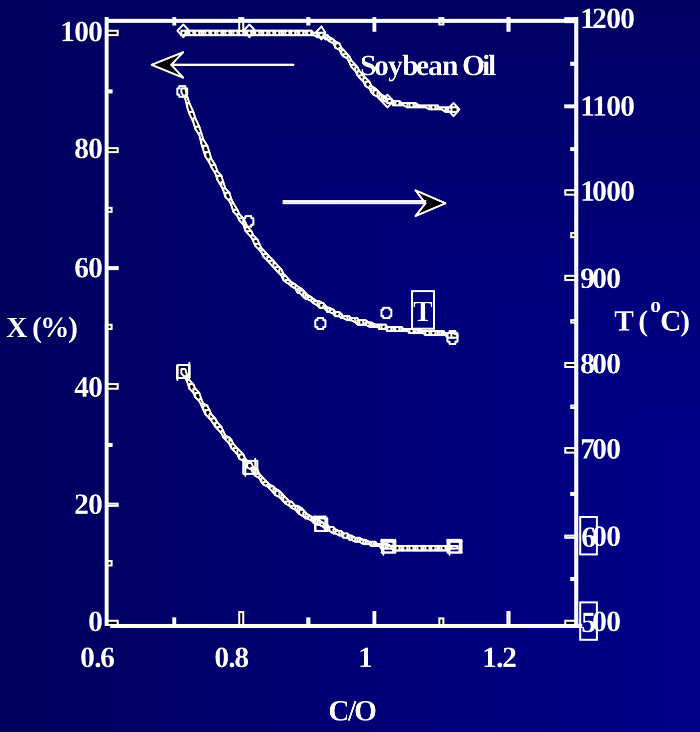
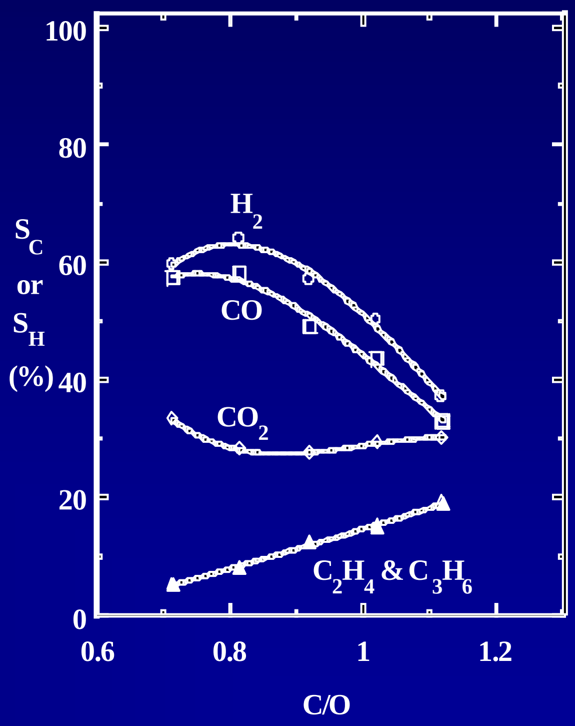
reactive flash volatilization
soy oil and sugar-water
<10 milliseconds
no carbon

Hydrogen and Olefins from Soy Oil

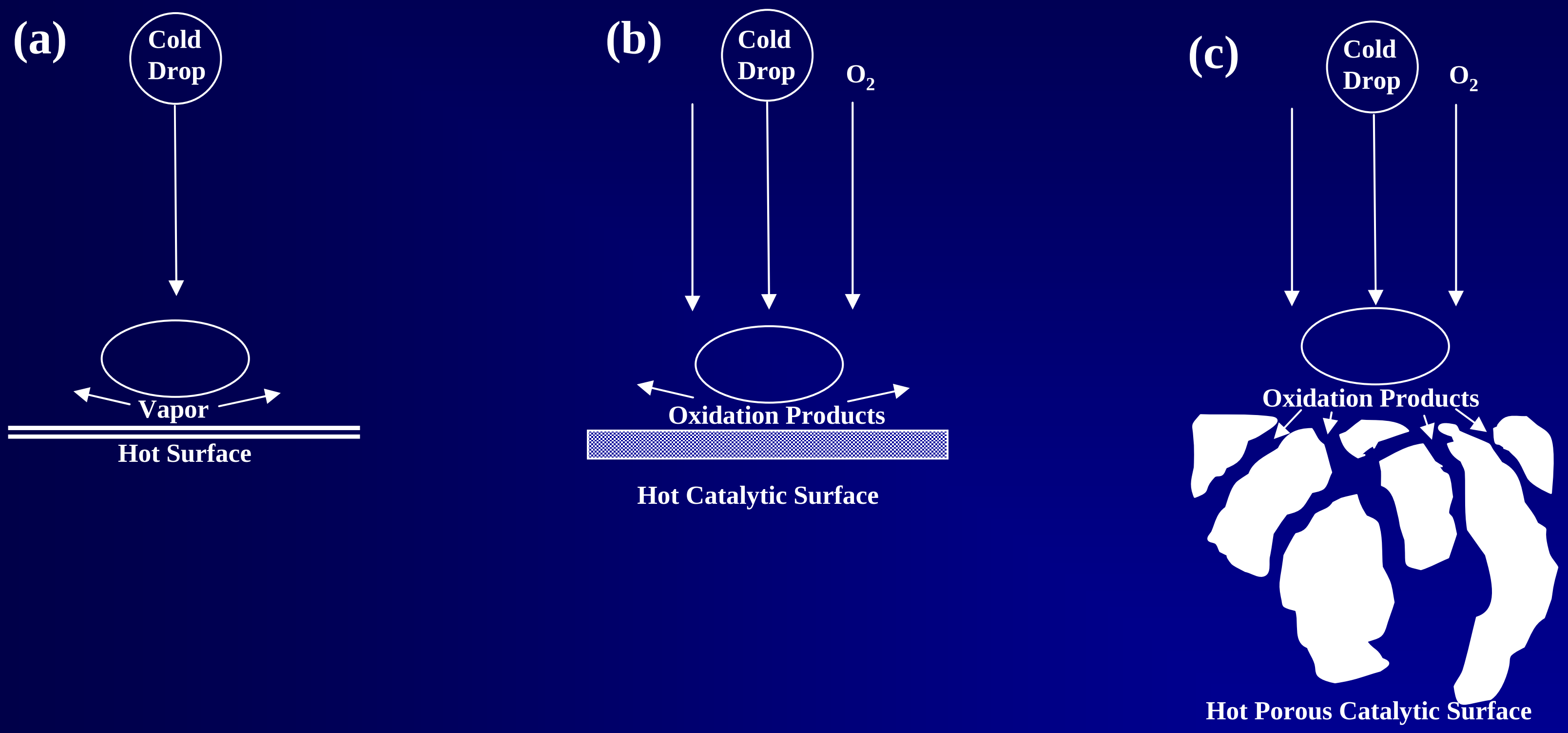
Reactive flash volatilization in <10 milliseconds
No carbon







Reactive Flash volatilization



Summary

Higher alkanes can be converted to H_2 and olefins

>80% H_2

>140% H_2 with steam added

80% olefins

50% ethylene and propylene

Alcohols and carbohydrates can be converted to H_2

steam reforming and partial oxidation

4 H_2 per C_2H_5OH

Biodiesel can be converted to olefins and olefinic esters

80% H_2

40% ethylene and propylene

ester linkage preserved

>20% olefinic esters

Additional Information

Significance of
"Renewable Hydrogen from Nonvolatile Liquids by Reactive Flash Vaporization"
by Salge, Dreyer, Dauenhauer, and Schmidt
Department of Chemical Engineering and Materials Science
University of Minnesota
November 2006

What happens if you overheat vegetable oil or sugar in your kitchen? Vegetable oil smokes and turns brown and sugar turns black. Both of these are caused by decomposition because oil and sugar will not evaporate, so they decompose to form carbon.

Schmidt and his students have found that, if you heat vegetable oil or sugar approximately one million times faster than you can do in your kitchen, they form no carbon at all, but rather form hydrogen and carbon monoxide. This gas mixture is called synthesis gas because it can be used to synthesize interesting fuels and chemicals such as synthetic gasoline. Since the mixture can be formed from biomass, this process can produce completely renewable fuels and chemicals.

This is the basis of a paper recently published in Science magazine.[1]

The largest obstacle to utilizing biomass as an energy source has been the absence of a process that can quickly and inexpensively convert it to a more useable fuel. The existing process called gasification converts biomass to a mixture of hydrogen (H_2) and carbon monoxide (CO) referred to as synthesis gas which can be converted into liquid fuels and chemicals such as methanol, dimethyl ether, synthetic diesel fuel, and ammonia. However, gasification is relatively slow, thereby requiring large, complicated, and expensive process equipment that must be centrally located.

Schmidt and coworkers have discovered a process that converts liquids into hydrogen and CO directly in a very simple chemical reactor that uses a catalyst to speed up the reaction. The process is simple, generates no carbon, and is fast enough to shrink the reactor by at least a factor of ten relative to gasification. They have demonstrated this capability using two common renewable feedstocks: vegetable oil and sugar-water.

The majority of biomass sources consist of large molecules that will not vaporize but rather decompose to form a low value solid char. This new process effectively chops the large molecules to smaller molecules that can react to form synthesis gas rather than solid char. The process was achieved using an automotive fuel injector that sprays tiny droplets of the liquid directly onto a glowing porous ceramic surface. The tiny drops impact the surface forming smaller drops which quickly break apart to small compounds that will react with air on the catalyst surface. The reaction with air makes the process operate at high temperature without the need of a heat source, thereby keeping the system very simple. Significant experimental challenges included developing an effective start-up procedure that suppressed flames and designing a reactor system capable of delivering

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[1] J.R. Salge, B.J. Dryer, P.J. Dauenhauer, L.D. Schmidt, *Science* **314,** 801, (2006).

fuel and oxygen to the catalyst for steady, autothermal operation. The small and simple design appears scalable and could potentially permit small-scale distributed biomass conversions systems on farms or large systems capable of transportation fuel production.

The new science in this project is the demonstration that small drops of liquid can impact a very hot surface and be converted into gases without causing carbon formation. In the absence of reaction on the surface, the drops would cool the surface, and a cold surface rapidly accumulates carbon that would stop the reaction. By coating the surface with catalyst (rhodium-cerium) and having oxygen present, the fragments from decomposition of the oil react with the oxygen on the catalyst surface to form hydrogen and CO and generate enough heat to maintain the surface hot. The steps in this process are extremely fast and complex: drops impacting the surface at high velocity, drop breakup into smaller drops, formation of a reactive vapor film between the drop and the surface, and penetration of fragments into the porous catalyst foam. All of this happens in thousandths of a second.

The potential technologies from this process arise because the process is extremely fast, at least a factor of ten faster than previous processes that rely on external heat to keep the surface hot enough for continuous reaction. We can use a catalyst to accelerate the process because we form no carbon that would otherwise cover the catalyst surface and stop the reaction. The use of a catalyst also allows considerable ability to "tune" the reactions to make more of a specific desired product such as olefins that might be used for production of polymers from renewable sources.

There is much work needed to turn technologies such as these into useful and economically viable commercial processes. Scaleup should be reasonably simple with no major changes in the reactor configuration required. The role of impurities and long term stability must be explored further. This technology has applications in use of biomass for hydrogen generation for fuel cells and, perhaps even more important, the generation of syngas for liquid fuels production. In the next decade processes such as this will undoubtedly come into the marketplace for production of renewable fuels and for hydrogen.