

- based on the assumption of very small mass exchange across the pycnocline, possibly limited to the rate of molecular diffusion [A. Lerman, *Geochim. Cosmochim. Acta* **31**, 2309 (1967)].
14. It is obvious that this circulation was curtailed since the mid-1970's with the gradual throttling of the Lisan Straits and the final disconnection of the southern basin in 1976; the Dead Sea has since become horizontally more homogeneous as indicated by temperature measurements.
 15. W. F. Libby in 1960 found an excess of 1 tritium unit (T.U.) in bottom waters; J. Houtermans in 1965 gave a value of 2.5 ± 0.2 T.U. at 300 m (off Ein Gedi) compared to 1.6 T.U. at a depth of 200 m (the latter sample was probably slightly con-

taminated during sampling). A profile taken off Massada in shallower water gave 5.08 ± 0.3 T.U. at 155 m (bottom); the surface tritium content at that time was 175 T.U. A similar trend can be observed in the 1978 profile in Fig. 2: bottom waters (at 300 m), 1.5 T.U.; waters at 240 m, 0.25 T.U.; and surface waters, around 20 T.U.

16. Measurements by H. Craig (1978).
17. Financial support was provided by the Israel-United States Binational Science Foundation (Project 936), the National Geographic Society, and the Minerva Science Foundation.

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Catalytic Production of High-Grade Fuel (Gasoline) from Biomass Compounds by Shape-Selective Catalysis

Abstract. Shape-selective hydrocarbon catalysis, such as the conversion capability of zeolite catalysts of the ZSM-5 type to produce high-grade gasoline from methanol, can be extended to produce a similar gasoline or aromatics from plant extracts. Examples are rubber latex, corn oil, and peanut oil. Novel mechanisms for shape-selective reaction sequences are demonstrated.

We have explored the use of molecular shape-selective catalysts (1) for direct and efficient conversion of high-molecular-weight biomass constituents to high-quality chemical components or fuel (gasoline).

The most talked-about biomass-to-liquid fuel scheme, and the only scheme

that is of major national commercial significance, is that for converting grain carbohydrates to ethanol. There is growing interest in such a process for displacing nonrenewable resources (petroleum and natural gas) by biomass crops. As described in greater detail elsewhere (2), the true productivity and true cost of the

net high-grade fuel in that case depends on the agricultural energy proficiency (that is, by how much the amount of high-grade fuel input initially invested in the agricultural effort is "amplified" by solar energy addition), and the efficiency of the conversion process (that is, the subsequent "attenuation" of the biomass energy in converting it to the high-grade fuel product). We are therefore interested in exploring highly efficient conversion technology.

It is common experience in the catalytic conversion of fossil fuel constituents (for example, petroleum crude fractions, coal liquids, and coals) that the efficiency of conversion to hydrocarbon fuels increases for organic compounds with higher hydrogen-to-carbon ratios and lower heteroatom contents. For this reason, biomaterials that are hydrocarbons or hydrocarbon-like are particularly interesting candidates for conversion to low-molecular-weight fuels or chemical raw materials. Calvin and co-workers (3) have proposed a search for plant species that generate a high proportion of hydrocarbon-like constituents. Buchanan and co-workers (4) have summarized a number of plant species that contain this class of material.

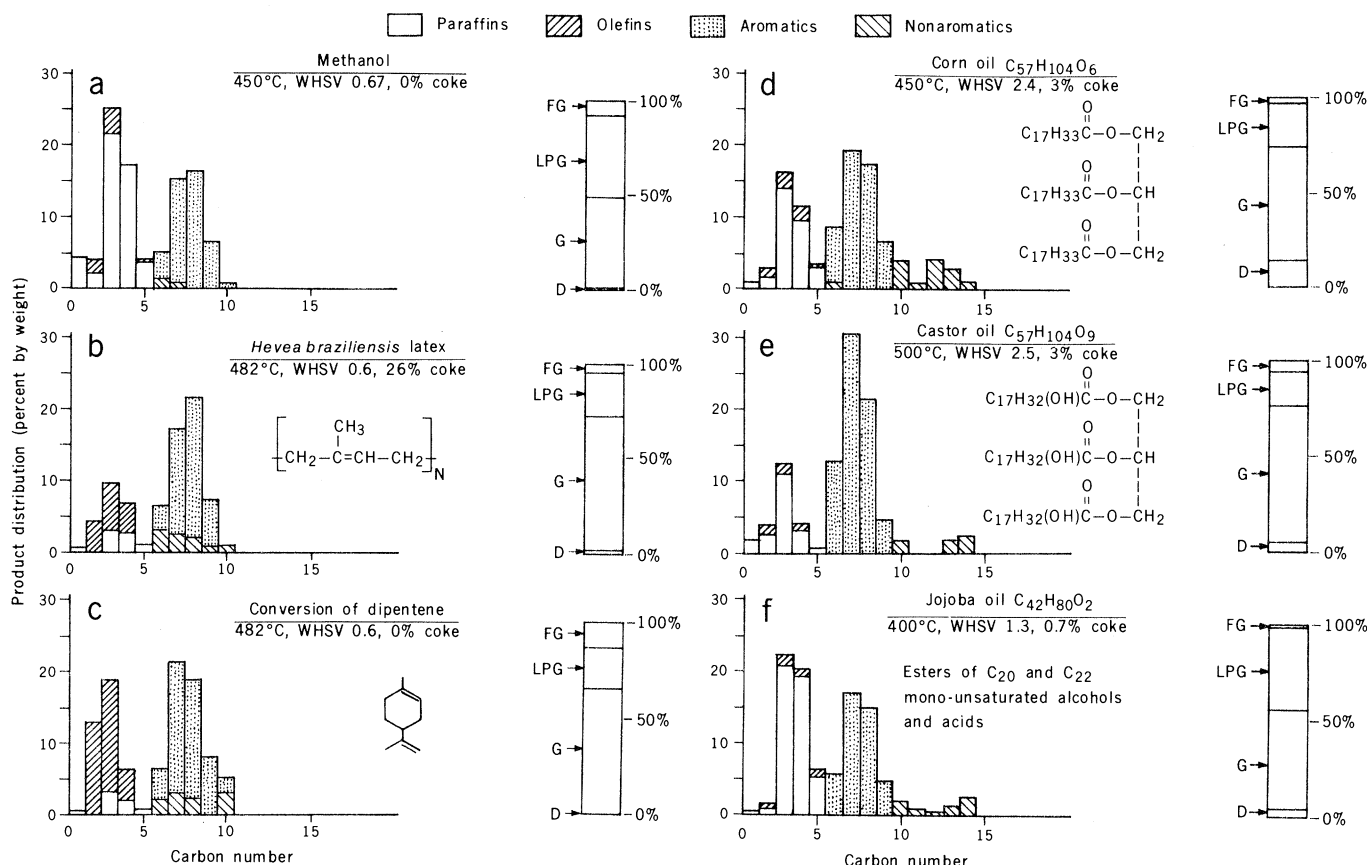


Fig. 1. Product spectra from catalytic conversion of methanol, and of various biomass constituents. The abbreviations FG, LPG, G, and D are for fuel gas, liquid petroleum gas, gasoline, and light distillate, respectively; WHSV is for weight-hourly space velocity.

Mobil's zeolite catalyst, ZSM-5 (5), of the family of highly siliceous porous tectosilicates (6) can convert methanol molecules selectively into hydrocarbon units with up to about ten carbon atoms per molecule. In fact, the compositional mixture is that of a high-grade gasoline (7). The selectivity results from the fact that the terminal size of the products (mostly aromatics) is limited by the molecular shape selectivity (8, 9) of the catalyst; that is, by the constraining size of the intracrystalline cavities.

We now find that this type of catalyst is also capable of efficiently restructuring biomass molecules into a very similar molecular weight-limited mixture of molecules. This occurs although the biomass-reactant molecules would appear too large to enter the catalyst cavities.

The natural product was fed with a piston displacement pump at a rate of 2 ml per hour with flowing hydrogen (300 ml per hour) over 2 ml of HZSM-5 catalyst (0.77 g, 14 to 30 mesh) contained in an electrically heated, vertical Pyrex reactor at atmospheric pressure. Liquid products were collected in a cold-water condenser, and gases were collected over brine. The products were analyzed by gas chromatography and gas chromatography-mass spectrometry (GC-MS).

For reference, Fig. 1a shows the products obtained in methanol conversion over this catalyst. Below this are the product spectra obtained in the conversion of rubber latex from *Hevea brasiliensis* (Fig. 1b); corn oil (*Zea mays*) (Fig. 1d); castor oil (*Ricinus communis*) (Fig. 1e); and jojoba oil (*Simmondsia chinensis*) (Fig. 1f). The products are listed by carbon number, as well as categorized as paraffins, olefins, and aromatics. For each case, the approximate percentage of product which corresponds to fuel gas (C_1 and C_2 compounds), liquefied petroleum gas (C_3 and C_4 compounds), gasoline, and light distillate (jet fuel, kerosene, or light diesel and heating oils), is also indicated. Peanut oil gave a product distribution very similar to that from corn oil.

In all cases, a high degree of conversion to BTX aromatics (benzene, toluene, xylenes), was achieved. The product mixture is similar to that obtained from methanol, and constitutes a high-grade gasoline with a research octane number (unleaded) of 90 to 96. The aromatics and light olefins could serve as valuable chemical feedstocks. The light fuel-gas production of methane and ethane is very low.

At first glance, the high catalytic conversion by this catalyst would appear to

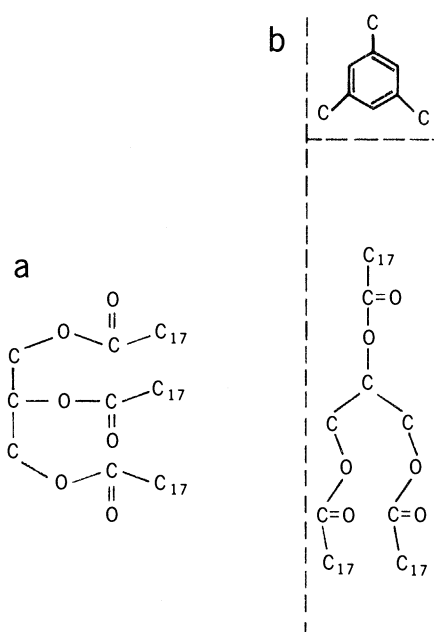
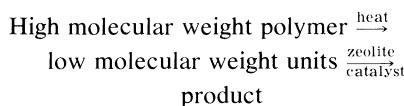


Fig. 2. Molecular structure of a triglyceride in (a) conventional display and (b) configuration that permits penetration into the zeolite channel. The effective size is compared to that of trimethyl benzene.

be inconsistent with its sharp molecular shape and size selectivity (7, 8), in that such large molecules would not be expected to penetrate the crystalline cavity.

However, results demonstrate (i) a novel kinetic mechanism for shape-selective catalytic products formation; and (ii) the need to revise our conventional concept of molecular shapes. The conversion of the natural polyisoprene rubber proceeds in two steps:



When the latex rubber is charged to an empty reactor at 400°C, we produce isoprene, dipentene (C_{10}), and C_{15} and C_{20} units. When we charge the major pyrolysis product, dipentene (C_{10})—or isoprene—directly to the ZSM-5 catalyst, we produce the product spectrum of Fig. 1c.

In the case of the high-molecular-weight triglycerides (peanut oil, corn oil) and esters (jojoba oil), the conventional mode of displaying such chemical formulas on paper, as shown in Fig. 2a, does not constitute the real spatial configuration of molecular structures. Aside from three-dimensionality, it ignores the flexibility in directional position of the various bond angles, as well as the continual dynamics of the entire structure.

Figure 2 will suffice to illustrate how the molecules in question can assume structural configurations for which the effective dimensions are no greater than those for a trimethyl benzene molecule. Trimethyl benzene molecules have been found (7, 10) to diffuse into the ZSM-5 structure with adequate facility to sustain useful catalytic conversion rates.

We have demonstrated that the capability exists, in principle, to convert efficiently a variety of biomass materials to high-grade fuel products or chemicals. This in itself, however, does not assure adequate net productivity of high-grade fuel generation (after debiting inputs of such fuels to the total agricultural-industrial effort). Here, the fraction of biomass that is convertible plays a most critical role (2).

We have also demonstrated an example for the shape-selective re-forming of large molecules by way of an initial thermal conversion to small-molecular-size intermediates which subsequently are restructured within a shape-selectively controlled zeolitic catalyst. Also, we show that certain high-molecular-weight organic molecules can dynamically "fold" to effective sizes capable of penetrating channels no larger than methyl benzenes.

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