

Electrochemical Key to the Biomass Store

by Professor James Utley

THE discovery and production on a large scale of materials based on organic chemistry, which is the chemistry of carbon compounds, has had an obvious and profound impact on modern society. They include most polymers and plastics, paints, dyes, pharmaceuticals, detergents, man-made fibres, perfumes and fuels. The carbon source we use is that which was originally 'fixed' in plants by photo-synthesis: on a geological time-scale, the carbon has been converted into oil and coal. It is these fossil fuels that are the feed-stocks of today's organic chemicals industry.

At first, organic chemicals industries relied on wood, grains and oilseed crops as feedstocks. Until relatively recent times fermentation was the main source of ethyl alcohol (otherwise known as ethanol); in Brazil it remains so and contributes significantly to the economy as a replacement for imported petrol. The earliest soaps, detergents and dyes, together with such chemicals as glycerol, methanol, acetone, turpentine and acetic acid, were all obtained from plant crops, which we call biomass. Paper, produced worldwide on an enormous scale, is derived from wood; cellulose, the main constituent of paper, was the starting material for the first man-made plastic (cellulose nitrate, 1862) and fibres such as rayon.

Plant crops proved to be an unreliable starting material, for their quantity and quality depended upon weather, pests and disease. Eventually they were replaced, by chemistry first based on acetylene from coal and then on ethylene from oil. Ingenious and economic routes to a great variety of organic chemistry developed. Many of the processes depend on the use of catalysts, chemical reagents which greatly speed up otherwise sluggish reactions. The first illustration makes simple comparisons of routes to acetaldehyde and acetic acid.

The oil crisis of the 1970s triggered a reappraisal. The world demand for organic chemicals is immense, amounting to hundreds of millions of tonnes every year. About 15 per cent of crude oil production is used for chemicals. Earth's reserves of oil must eventually be exhausted, though opinions vary widely about when this will become critical. A large amount of coal remains to be used but it only postpones the problem and the economics of a coal-based organic chemical industry will certainly differ from those of the present oil-based one.

In contrast, biomass is a renewable resource. Modern methods of crop production and protection (thanks again to clever organic chemistry) ensure that the raw materials are cheaper and more reliable.

The application of genetic engineering is producing crops that mature quickly and resist disease. And we now know that biomass production could comfortably keep pace with the demands of the industry. Within the biomass resource, forest trees are the largest renewable carbon source; sugar cane is also high on the list and is remarkable for being the most efficient device for the photosynthetic

conversion of carbon dioxide into stored organic chemicals. polymers called lignins, which are not fibrous but cross-linked to give strength in three dimensions. In the tree it is bound to cellulose. In the production of paper pulp the lignin and cellulose are separated, the cellulose component is used, and at present about 75 per cent of the lignin residue is burned or discarded, sometimes as a polluting effluent. Some 39 million tonnes of lignin are produced annually in this way. Yet lignins are polymers composed of

derivatives of the most important aromatic hydrocarbon, benzene. Coincidentally, the petrochemicals industry produces from other hydrocar-

essence. Although it was originally obtained by extraction from the vanilla bean, an important route to it is now by degradation of lignin. It is done chemically, but the conditions needed to break down lignins are severe. This is not surprising because, although not every structural detail of lignins is understood, they are known to be complex and tripartite, with the monomeric parts linked together by strong carbon-oxygen and carbon-carbon bonds. Lignins isolated from wood might easily consist of 150 or more such units; the accompanying diagram of its partial structure illustrates the complexity of the molecules

The ability of certain fungi and bacteria to rot wood has recently been shown to involve natural catalysts called oxidising enzymes. In this context we use the most fundamental definition of oxidation, the removal of electrons. Removing electrons from lignins is also the way chemical oxidising reagents attack, but in the laboratory or chemical plant concentrated reagents and temperatures in the region of 200°C are required compared with the modest temperatures and pressures at which nature does its chemistry. Despite the apparent advantages of enzymic oxidation and the disadvantages of existing chemical

ries, has been concerned with the mechanisms of electro-organic reactions. It was natural, therefore, that the two topics should become linked. But why should oxidation be the chosen technique for breaking key chemical bonds in lignin?

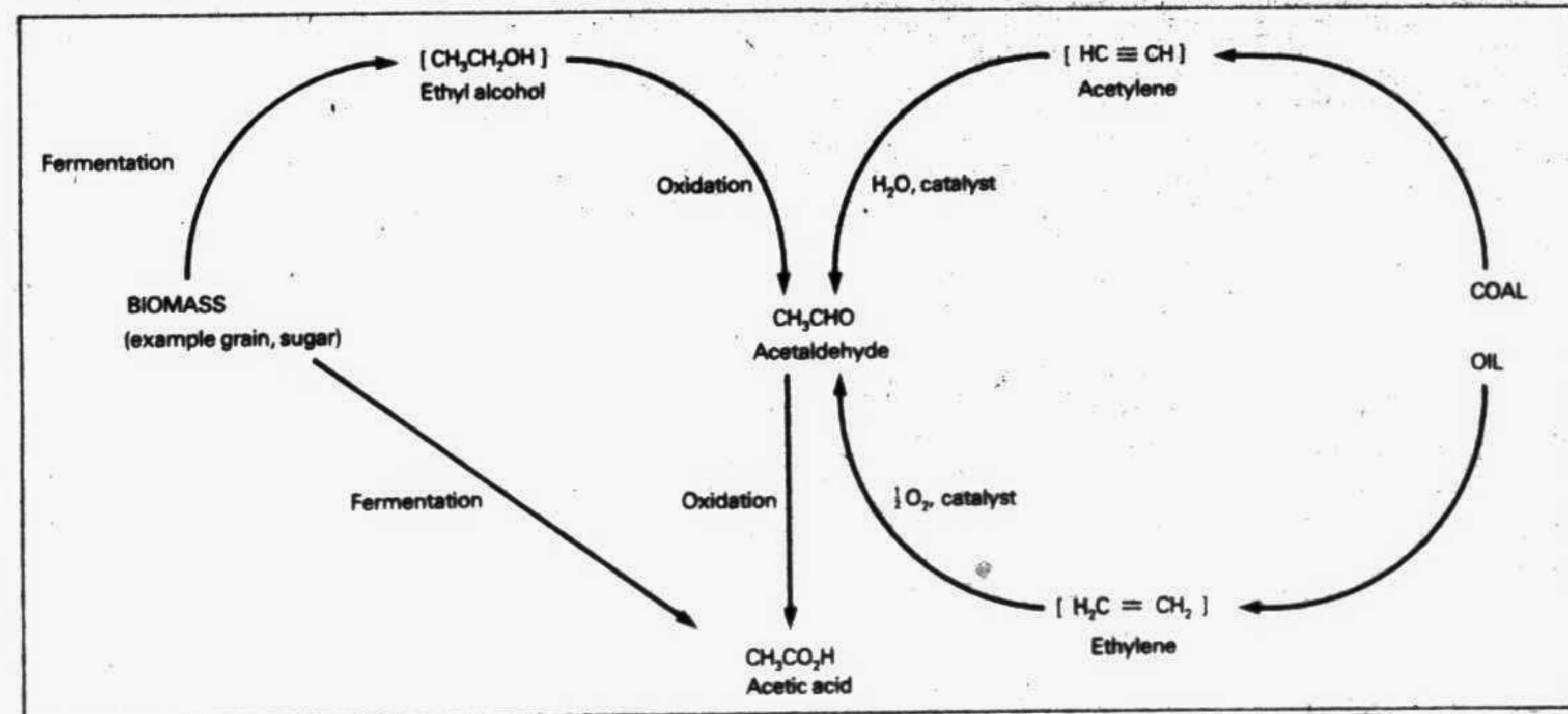
The chemical bond is essentially the sharing of a pair of electrons by the two bound atoms; in addition certain atoms such as oxygen possess extra pairs of non-bonding electrons.

Removal of electrons from a stable molecule will therefore weaken its overall bonding and it may fragment at the most weakened bonds.

In electrolysis, electrons are removed at the posi-

In electrolysis, electrons are removed at the positively charged electrode (anode) and added at the negatively charged electrode (cathode). The most common type of bond holding the benzenoid units together in lignins is a carbon-oxygen bond at the betaposition.

Examples of organic syntheses based on biomass and on coal or oil.



conversion of carbon dioxide into stored organic chemicals.

Chemical Treasure House

Wood, straw and bagasse (spent sugar cane) are the chief lignocellulosic materials available for conversion into useful organic chemicals. The organic chemist views a tree as potentially a very useful mixture of chemicals. Of these, the natural polymer cellulose is a fibre (such as in cotton) and it has little mechanical strength. The great strength of a tree derives from other natural

bonds roughly the amount of benzenoid compounds that is thrown away as lignin! These benzene derivatives are the building blocks for familiar materials that include polystyrene, terylene, plastic foams used in furniture upholstery, adhesives, detergents, paints and many others.

About five per cent of lignin is converted into useful chemicals.

A good example is the formation of vanillin, the fragrant component of vanilla

and the major linkages which must be broken to give benzene derivatives, including vanillin. The precise structure of a lignin depends on the species from which it is obtained. In view of the demand for benzene-derived compounds, what a waste it is to burn such a polymer as lignin, carefully constructed in nature with an efficiency and selectivity that the laboratory chemist seldom achieves!

Degradation and Electrochemistry

techniques, the useful enzymic depolymerisation of lignins on a large scale is far from a practical proposition.

Perhaps the most interesting feature is that reaction in both chemical and enzymic degradation is initiated by electron transfer.

Electrochemistry has primarily to do with electron transfer and in recent years a great deal of fundamental chemical research, including ours at the Queen Mary College laborato-

Scientists Differ on Oil Slick Impact

Differing opinions are held by scientists on how exactly a major oil slick from the Persian Gulf is likely to affect marine life in Indian waters — whether it will cause a serious loss of fish stocks or whether it could, eventually, enrich the sea and boost the underwater life-cycle. by Prakash Chandra

INDIAN scientists and government officials are apprehensive over the impact of the oil slick which resulted from the destruction of Kuwaiti refineries during the Gulf War.

The slick is now spreading across the Arabian Sea and may hit India's western coasts. One scientist said, "Much of this spilled oil will be converted into tar balls which will float along to hit the northwestern part of the Indian coast some time this summer."

Dr N. Prasad, a senior official at the Department of Ocean Development, says it is possible the tar balls will drift later into the Bay of Bengal and damage fishery and marine resources along India's eastern coast as well.

Scientists are not sure how the oil spill will affect the availability of microscopic marine nutrients in the area. Environmentalists fear an ecological disaster in the near future because some of the Kuwaiti oil refineries destroyed in the Gulf War are still aflame.

A senior Indian scientist told Depthnews, "We have observed that 40 per cent of the spilled oil has already evaporated into the atmosphere, leaving behind a slick that is undergoing a natural process of degradation. Half of this eventually will get converted into tar balls which keep floating on the surface of the water. The other half gets into the marine food chain causing great damage to aquatic life forms."

Indian scientists are divided on the question of how exactly the oil spill will affect marine life. While some experts believe India is facing a possible fish shortage, others

think the slick is a blessing in disguise.

Optimistic scientists believe hydrocarbons and other components of oil provide nourishment to a large number of marine microorganisms eaten by fish. As these microorganisms proliferate, other aquatic life forms, including fish, are expected to thrive as well, thus theoretically boosting potential sea food production in India.

It has been observed that microorganisms in water columns and sediments of the ocean are found to be in abundance only when the level of hydrocarbon concentration is high. Most of these organisms constitute an important link in the food chain and in the productivity cycle of marine life.

Oil is also a source of carbon necessary to the life cycle of microscopic plants in the sea. Hydrocarbons provide the nutrients cycled by bacteria which are necessary for the growth of minute marine plants. In view of this, an excess of hydrocarbons in water may be a positive factor in the natural processes of the marine system.

This point of view seems to be borne out by a "creel census" conducted in the Corpus Christi Bay in the United States. The survey revealed that the region around oil platforms yielded the highest catches for sports fishermen.

Similar results were also revealed in another study on the Louisiana Continental Shelf, also in the US. It was observed that the fish yield over an extended period of time was directly proportional to the production of oil in the area.

Other studies tend to sug-

gest that the slick may have some negative effects in the short term but may be beneficial in the long run.

Some marine scientists in Bombay believe it is likely that microscopic marine life would die at the initial strike of the oil slick as they would be deprived of sunlight. This would result in less or on nutrients for fish.

After some time, however, when oil has been broken up into fatty acids and glycerol, the food chain would be strengthened and therefore the plankton population will rise rapidly. This would lead to a potential boom in fish production.

It is also quite likely that some kind of alteration or mutation of marine species could occur after the degradation process. An American researcher found that adult mussels taken from Coal Point in California registered higher survival rates on exposure to oil in an aquarium. Similarly, adult lobsters displayed positive feeding responses to substances soaked in fatty materials from petroleum.

Still, Indian officials prefer to be safe than sorry. The Indian government is definitely not waiting until the slick manifests its effects — whether positive or negative — before acting.

Several government agencies have already been given instructions to monitor the oil slick when it does reach India's offshore areas. These include the Ministry of Environment and Forests, Ministry of Surface Transport, Office of the Director-General of Shipping, Port Trust Authority and the Coast Guard. State governments have been asked to report immediately changes in marine ecology. — Depthnews

ADVERTISING is one component of the US nuclear industry's co-ordinated communications programme aimed at assuring an understanding of nuclear energy's role and benefits. This communications programme, conducted by the US Council for Energy Awareness (USCEA), includes many media and public relations activities, a variety of publications aimed at key audiences, reports, technical analyses, as well as advertising.

Advertising enables USCEA to disseminate key information to very broad audiences continuously and consistently.

USCEA's advertising programme began in 1983. It is aimed primarily at opinion-leaders and decision-makers, but it reaches about 160 million Americans (most of the US population) at an average of 10 times each year. The advertising runs on national television, in major magazines (Time, National Geographic,

The Economist, and many others), and in newspapers (The Wall Street Journal, the New York Times, and the Washington Post). Research shows that there is a synergy between the television and print advertising. In fact, the advertising is designed to promote such synergy. People who are exposed to USCEA's television commercials are more aware of the print ads than people who are not exposed to the commercials.

Testing shows that USCEA's advertising programme works. In fact, USCEA's 1989 ad campaign tested five times better than the norm for corporate advertising. In addition, evaluation research with large nationally representative samples shows that there are more positive attitude changes among people who are effectively reached by the advertising (i.e. those who remember it) than among others in the population.

Research and testing are the foundations of USCEA's entire communications programme, including the advertising effort. Effective communications depend on knowing what the public thinks and what information is needed to inform the public. USCEA's research has four

Advertising as a Communications Tool

by Edward L. Aduss and Ann S. Bisconti

elements:
● First, through national surveys and polls, USCEA monitors public attitudes, priorities, and concerns about energy issues.

● Second, USCEA conducts strategic research and message testing, to identify the most effective points that can be made among the many available.

● Third, USCEA tests its ads to measure their ability to

get attention and convey the intended message in a positive and meaningful way.

● Fourth, USCEA conducts continuous evaluation research to learn about the overall effectiveness of the advertising programme. Large national samples are surveyed twice to find out about influences on attitude change.

USCEA's advertising programme has helped maintain a favourable public opinion envi-

ronment nationally for nuclear energy plant operations in the United States and for building more plants in this country when they are needed. In addition, the national advertising supports local communications by electric utilities.

The advertising has also created a reservoir of support in difficult times.

For example, research surveying the same

people before and after Chernobyl found that those who remembered seeing USCEA's pre-Chernobyl advertising were much less affected by the accident than others who had not been so informed.

Having the advertising programme in place gives USCEA the capability to respond to special situations quickly and effectively.

A television commercial sponsored by the US Council for Energy Awareness artistically depicts price and supply fluctuations that have occurred in oil markets and emphasizes the importance of electricity produced from coal and nuclear energy.