Carbon dioxide recycling

John A. Glaser

Published online: 25 August 2009
© Springer-Verlag 2009

The recycling of carbon dioxide to methanol and dimethyl ether is seen to offer a substantial route to renewable and environmentally carbon neutral fuels. One of the authors has championed the “Methanol Economy” in articles and a book. By recycling ambient CO_2 , the authors argue that we do not contribute new GHG to the atmosphere but remove a quantity for a short time period. Methanol is extolled for its combustion characteristics and proved utility as a fuel in internal combustion engines. Syngas sources from the water gas shift reaction are considered as a means of current methanol manufacture. Reaction strategies leading to dimethyl ether and higher molecular weight organics are scrutinized. Hydrogen production is a very important component of the scheme to use CO_2 . Many of the conversion techniques for hydrogen gas are highly endothermic which leads to energy costs to conduct the conversion. Energy to drive the cycle is derived from available forms of renewable energy such as solar, wind, hydro, geothermal and oceans. This carbon neutral cycle perspective requires further elucidation of the connection of the reaction components at production scale. It is good to see established chemists trying to organize solutions to the current fuel crisis.

(J Org Chem 2009, 74, 487–498)

Decision analysis tool to synthetic route selection

For a host of reasons, it is important to test the synthetic route to fine and pharmaceutical chemicals. Costs, safety, and greenness are among a range of targets that can be fundamental to synthetic route selection. Researchers at Astra-Zeneca have provided insight into their use and application of decision analysis to aid synthetic route selection. Kepner-Tregoe decision analysis has been applied to a wide variety of business over the past 50 years. The practice of this analysis is derived from research conducted by the Rand Corporation focused on strategic decision making. The broader applications of the analysis system are available on the web at <http://www.kepner-tregoe.com/>. For the synthetic route selection application, the process can be specified in a series of interlinked steps: decision statement, objective development, musts and wants identification, wants weights, alternatives generation, align wants with musts, screen alternatives with must criteria, score alternatives

J. A. Glaser (✉)
US Environmental Protection Agency,
National Risk Management Research Laboratory,
26 W King Dr, Cincinnati, OH 45268, USA
e-mail: Glaser.John@epa.gov

on want criteria, adverse consequences identification, and selection of best balanced choice (see following scheme).

The decision statement is particular to the synthetic target. Objectives are selected from categories such as safety, intellectual property issues, difficult step accommodation, raw material costs, proposed chemistry feasibility, the number of steps required to reach the target, steps to a key step, and flexibility. The objective can then be filtered into the two categories of musts and wants. To provide a rating of the synthetic route, the wants are endowed with weights to enable the selection process. The alternatives are then measured in reference to the wants. The remaining candidate synthetic routes are evaluated for adverse consequences and the best balanced choice(s) emerges. *Org Process Res Dev* 2008, 12:1041–1043.

Synthetic route selection

Application of this decision template has been applied to the synthesis of AZD7545, an inhibitor of pyruvate dehydrogenase kinase (PDK) designed for oral treatment of type II diabetes. A synthetic route generation paper exercise led to the formulation of more than 40 potential routes. Available resources reduced the target number to 3–4 routes that could be investigated in detail in a 3–4 month period. A total of 12 routes were assessed in some detail by laboratory experimentation. One default factor was the stipulation of a route permitting the manufacture of 1 kg with a possible extension to 10 kg. The expense of the chiral acid was a strongly guiding factor due to cost. Synthetic strategy was directed to incorporate the costly chiral acid at later steps of the synthetic route to avoid the losses incurred from the synthetic yields of steps earlier in a given synthetic route. The synthetic route scoring template accompanies the paper. The interplay of the synthetic chemistry and decision analysis is very interesting and the commentary of the paper shows the importance of such an interaction for fine and pharmaceutical chemicals.

(*Org Process Res Dev* 2008, 12(6), 1044–1059)

Alternative route selection

A structure target AZM 574670 was proposed as an alternate to AZD7545 as a PDK inhibitor. In a similar fashion synthetic routes for AZM574670 were assembled. The synthesis project was stopped due to toxicology results. Selection of a single route for long-term production was not completed. The synthetic details with accompanying musts and wants strengthen the insight into the utilization of the decision analysis. It would be interesting to see how alternative decision analysis and strategy compares to this eye-opening effort. The research people and the firm should be commended for their desire to share their implementation of the decision analysis.

(*Org Process Res Dev* 2008, 12, 1060–1077)

Hamburger energy costs

Seldom does a consumer regard the consequences of their consumption of foods or materials. Energy misuse and food displacement are some of the contributing factors associated with the negative aspects of food selection. According to the 2006 United Nations Food and Agriculture organization report, the meat in our diets is a large contributor to greenhouse gas production. This article uses very clear graphic depictions to underscore the consumption of beef in hamburgers and its effects on issues of global concern. It is amazing to consider the annual beef consumption per capita numbers varying from 120 lbs in Argentina and 92 lbs in the US to Moldova where consumption is 22 lbs per year. As the taste for beef across the globe changes to increased per capita intake we will face continuing severe environmental problems. The CO₂ emission equivalent for edibles can give a sense of the problem. For an automobile achieving 27 miles per gallon, the carbon dioxide equivalent emissions per 0.5 lb of edible are the same as driving the auto 0.17 miles for potatoes, and a whopping 9.81 miles for beef. An analysis of beef production shows that emission are 40% for feed crops, 32% for emissions from cattle and their waste, 14% from general farm production, and 14% for fertilizer production. With world beef production increasing at a pace of 1% per year strain will be placed on production systems. It becomes very important to properly design and operate economically efficient feedlots to reduce GHG emissions. Beef consumption is rising globally and will become a stronger contributor to GHG emissions with the enhanced demand. *Sci Am* 2009, 300(2):72–75; *Ecol Econ* 2008, 67(3):412–419.

World food supply impact from biofuel production

A group of analysts provide inspection of the various forms of biofuel production in terms of the use of fossil fuel, land and water resources. Food supply and malnourishment, world cropland resources, water resources, and energy resources are scrutinized in an extensive analysis of biomass resources and conducted on topics such as corn ethanol, grass and cellulosic ethanol, methanol, soybean diesel, rapeseed and canola diesel, oil palm, jatropha, and oil production from algae. This group has distinguished itself and its leader as major naysayers for biofuels efforts. The clarity of the analysis and explicit assumptions offer some insight to the analysis process. In each case according to this group biofuel production is inefficient and does not return equal or more energy to energy use for conducting the biofuel conversion. One troublesome quality of the various analyses is that side

products such a glycerol from biodiesel production and waste carbon products used as steam fuel are not credited to the production process. Water resource requirements cited in the article are a bit puzzling. Corn production of 200 bu/acre generally requires 22–26 acre inches of water for most of the corn belt which is considerably less than the 700,000 gallons required by this article. It is important for the analysts and users of this information to understand the dimensional sensitivity of these model estimates and their interpretation. *Energies* 2008, 1:41–78.

Too much light!!!!

Dramatic photographs show the effects of light intrusion into the nighttime of much of the globe. A nighttime map projection based on satellite and ground data evaluation of scattered light in the timeframe of 1996–1997 shows three large areas of eastern United States, Europe, and Japan as very large light pollution areas. Calculations indicated that two-thirds of the globe's population lives under light polluted skies and one-fifth cannot see the Milky Way. Light pollution upsets the light rhythms of humans and other life forms. Humans are diurnal creatures despite our attempts to engineer conditions rejecting the notion. Studies have identified the light pollution to be a product of poorly designed lighting fixtures that permit light to shine upward into space rather than directing to light intensity towards the earth. Simple redesign of the fixtures to direct the lighting intensity to the earth has significantly reduced the light pollutions in areas where the new design has been adopted. Human reaction to changes to the diurnal cycle can lead to illness and poor adjustment during the work day. Our biological welfare requires darkness to preserve the natural oscillation of waking and sleep as part of one of our circadian rhythms. Birds, turtles, bats, and other animals are sometimes misdirected by the light pollution to their detriment.

It is reprehensible that the vast quantities of energy supporting the light pollution cannot be redirected to less profligate uses. *National Geographic* 2008, 214(5):102–123.

Ecological and human health effects

Forms of light pollution are sky glow, light trespass, glare and over illumination. Noticeable ecological effects of light pollution have been reported. State of Florida wildlife authorities have documented the effects of light on adult turtles and their hatchlings. Toronto has documented 42,000 bird collisions with buildings since 1993. The bright lights and highly reflective glass surfaces are seen to

contribute to the confusion of migrating birds and their nocturnal migration patterns. Wildlife authorities are concerned that the habitat of many animals will be lost without the protection of night. Human populations have shown sleep disorder effects when work schedules interrupt the natural circadian clock of individuals. The effects of such disruption has been connected to medical disorders such as cardiovascular disease, cancer, insomnia and depression. Some 10–15 percent of our genes are controlled by the circadian cycle. Disruption of the cycle is expected to lead to health problems. *Environ Health Perspect* 2009, 117(1):A20–A28.

Smarter lighting

Light pollution will remain a contentious issue until some effort at providing the underlying definitions occurs. A major hurdle is the desired balance between light pollution and useful lighting. How can one quantify lighting objectively to test whether the desire balance is achieved? Criteria are now being considered by professional groups leading to the development of proper measures of lighting design and the conservation of energy. The polluting light can be easily characterized as unnecessary non-renewable energy resource exploitation and the accompanying GHG emissions. In the US some 8–9% of the electricity is consumed by lighting applications. An estimated 17.4 billion kilowatt-hours generated by fuel having the energy content of 186.3 trillion BTU is wasted each year. One major component of this waste is the upward radiation of light leading to light pollution. Just to emphasize the dimensions of the waste, the wasted energy is equivalent to the combustion of 9 million tons of coal or 32 million barrels of oil. *Environ Health Perspect* 2009, 117(1):A28–A31.

Flash estimate of CO₂ emissions from energy sources

The US Energy Information Administration has recently reported in its report, U.S. carbon dioxide emissions from energy sources 2008 flash estimate that US energy-related carbon dioxide emissions declined 2.8 percent in 2008 due to the struggling economy and higher energy prices. The report revealed that U.S. energy-related emissions decreased 165 million metric tons, from 5,967 million tons in 2007 to 5,802 million tons in 2008. The all-time peak price levels for gasoline and diesel led to reduced demand assisted by a drop in consumer income. Electric power sector emissions decreased by 50 million tons, or 2.1 percent, in 2008. Electricity generation declined by 1 percent. Petroleum combustion emissions decreased by 155 million tons, or 6 percent, and natural gas combustion emissions

increased by 13 million tons, or 1.0 percent. Coal combustion emissions decreased by 23 million tons, or 1.1 percent.

<http://www.eia.doe.gov/oiaf/1605/flash/pdf/flash.pdf>.

Increase of global greenhouse gas emissions

For the time span of 2000–2005, the European Commission showed that global annual man-made greenhouse gas emissions increased 15 percent which is an increase over the 6 percent rise recorded between 1995 and 2000. Carbon dioxide-equivalent emissions from man-made sources in 2005 totaled 41 billion metric tons, up from 33 billion metric tons in 1990, and 24 billion metric tons in 1970. This data is derived from the Commission's Joint Research Center and The Netherlands Environmental Assessment Agency, as part of the Emission Database for Global Atmospheric Research, or EDGAR project. The EDGAR data set is unique to the 35 years period (1970–2005) showing greenhouse gas emissions as a function of country and emission sector. The EU anticipates that this dataset can be a pivotal component to the Kyoto protocol successor.

The dataset shows industrializing country emissions have increased most dramatically, from 7 billion metric tons in 1970 to 21 billion metric tons in 2005, and at the same time, emissions from developed nations have risen from 16 billion to 19 billion metric tons. <http://edgar.jrc.ec.europa.eu/>.

Publishing collaboration gone awry

Recent information has disclosed that The Australasian Journal of Bone and Joint Medicine was invented to support Merck drugs and published by Elsevier. It is reported that the journal was supported entirely by Merck funding. Published on the early 2000s, the journal was composed of news, reprinted journal articles, and unsigned reviews. Australian doctors were the targeted audience for this journal. This effort has been described as “stealth marketing....under the guise of a regular journal”. This report asserts that Merck has not admitted to any responsibility in the matter and pointed to Elsevier as the appropriate respondent to questions. Elsevier has responded professionally and admitted that there are six different faux journal titles in a series related to the journal in question. Elsevier has admitted that “this was an unacceptable practice” and has conducted internal review discover details of operation that are not commensurate with its publishing philosophy. Merck appears to have sloughed responsibility to the publisher without admitting complicity. Some collaborations between business and publishers

can be highly desirable but any effort must admit openly to the terms of the effort and possibly identify the collaboration as sponsored endeavors. If publications do not aspire to a higher level of ethical behavior then there will be little means to discern the true information of publications. The Scientist, 2009, 23(6):13

New journal

The new journal Sustainability is an international, peer-reviewed Open Access journal considering environmental,

cultural, economic and social aspects of sustainability. A series of more than 20 sections and special issues are planned of topics ranging from green chemistry to land use. Publication fees will be waived for 2009 submissions. This journal should be of general interest to the readership of Clean Technologies and Environmental Policy. <http://www.mdpi.com/journal/sustainability>.