

be used by itself to predict storage stability. It is the detailed structure of the individual nitrogen compounds and the interactions they undergo with other reactive species which influences the overall sediment forming process.

Acknowledgment

Analytical work was carried out by W. K. Robbins.

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Received for review August 23, 1982

Accepted February 22, 1983

This work was sponsored by the Department of Energy under Contract DE-AC19-79BC10045.

Norbornadiene-Quadricyclane System in the Photochemical Conversion and Storage of Solar Energy

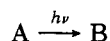
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Experimental data are presented on the photochemical conversion of norbornadiene to quadricyclane. Parameters examined in the efficiency and kinetics of conversion were concentration effects and the presence of solvents and photosensitizers. A model of a flat-plate, batch, photochemical solar collector was evaluated with the experimental data and insolation information. Process analysis and preliminary economic evaluation of the system are presented which point to the conclusion that the system is technically feasible but economically noncompetitive at present.

Introduction

Photochemical conversion and storage of solar energy, in particular by valence photoisomerizations of organic molecules, has recently aroused the interest of various laboratories around the world (Jones et al., 1979; Hautala et al., 1977; Laird, 1978; Scharf et al., 1979; Lane et al., 1977). Several reviews of the subject have been presented in international conferences (Lichtin, 1974; Bolton, 1977; Hautala et al., 1979) which have depicted the main advantages and problems associated with such photochemical systems. The fundamental properties of such a photochemical system have been outlined, although systematic testing or economic evaluations are scarce (Hautala et al., 1979; Jones and Ramachandran, 1976). The constraints imposed on the system include the following. (1) The endergonic photochemical reaction



should be neat, with a yield greater than 99% and an enthalpy of reaction greater than say, 500 J/g. (2) Chemical A (with or without a sensitizer) should absorb a large percentage of the photochemically effective solar spectrum range between 300 and 700 nm. Engineering efficiency of absorption should be high too, perhaps approaching the maximum possible of 12%, as indicated by (Bolton, 1977). (3) Compound B should be stable at temperatures below

the thermochemical range of the reverse reaction $B \rightarrow A$. This reaction should be neat, with a yield greater than 99%, thermally or catalytically induced. (4) The normal boiling points of compounds A and B should not be lower than, say, 80 °C. The freezing points should be lower than, say -10 °C. The compounds should be nontoxic, they should present no major safety hazards, and they should be safely stored and transported. (5) Reactant A should be relatively inexpensive.

The restrictions imposed, particularly by the first three constraints, are severe. In particular, the overall storage efficiency as calculated by Scharf et al. (1979) is very low indeed. Research work and systematic testing and screening of the compounds is still at a low pace. In particular, no field results have been reported yet, although there were some indications (Hautala et al., 1979) that work with the norbornadiene compounds is in progress.

The norbornadiene-quadricyclane system appears to date to offer the best possibilities (Jones et al., 1979; Hautala et al., 1979) as seen from Table I. Work is being carried out to extend the range of absorption of the solar spectrum and to improve the storage efficiency (Jones et al., 1979).

The purpose of this paper is to present experimental data on the photochemical kinetics and efficiency of the norbornadiene-quadricyclane system and to evaluate

Table I. Characteristics of Known Photochemical Systems for Solar Energy Storage

compound A	compound B	ΔH_{isom} , J/g	quantum efficiency, Φ_B^A	overall storage efficiency, η_c	λ_{ground} , (nm)	back reacn temp, °C
1. norbornadiene (sens. acetophenone)	quadricyclane	1190	0.9	0.0023	366	135-200
2. norbornadiene (sens. CuCl)	quadricyclane	1190	0.4	0.0021	388	135-200
3. dimethyl 2,3-norbornadiene dicarboxylate (sens. benzophenone, camphorquinone)	dimethylquadricyclane dicarboxylate	372	0.5	0.0002	366	115-180
		372	0.3 (0.6)	...	480	115-180
4. dicyclopentadienone (in solvent)	bishomocubane	500	0.4	0.0007	366	140-180
5. <i>trans</i> -diacetylidigo (sparingly soluble)	<i>cis</i> -diacetylidigo	100	0.2	0.0095	610	low
6. dicyclopentadiene (photosensitized)	bishomocubane	500	(0.4)	...	(290-400)	-120?
7. 1-alkenyl-2-pyridone (in aqueous solution)	Dewar pyridone	300-339	...

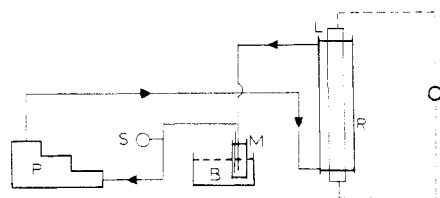
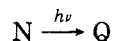


Figure 1. Diagram of the experimental apparatus: L = lamp; low pressure Hg 15W; R = reactor; M = mixer; P = pump; B = constant-temperature bath; S = sample point.

preliminary process economics in view of the collected data and a theoretical model of the process.

Experimental Section

Apparatus. Our main purpose was to investigate the kinetics of the photochemical reaction



The experimental apparatus is shown in Figure 1. The reactor was a cylindrical UV low-pressure Hg lamp surrounded concentrically by a glass tube. The photosensitive liquid flows in the annulus. Since the system was to work in a batch-recycle mode, the reactor was connected to a mixer by a positive displacement pump. The liquid in the mixer was agitated by a magnetic stirrer. The mixer itself was placed in a constant-temperature bath. Samples of liquid were withdrawn from the mixer and analyzed chromatographically.

The reasons that led us to this specific design were (a) the need for monochromatic radiation (254 nm) with a rather high incident intensity; (b) the fact that for a significant conversion, large residence time was required; (c) easy sampling.

Treatment of Data. Axial and radial dispersion in the reactor were ignored. Instead the liquid is supposed to flow in the reactor in the form of annular rings. Each of these rings is considered independent of the others (chain-like flow). The radiation from the lamp is considered monochromatic at 253.7 nm, since this lamp emits over 90% of its UV intensity at this wavelength.

Since the isomerization reaction is photosensitized, the quantum factor Φ is expected to be dependent on norbornadiene (N) concentration. This factor Φ is defined by

$$\Phi = \frac{\text{quanta leading to N dissociation}}{\text{total absorbed quanta}} \quad (1)$$

Thus, the reaction rate is expressed as

$$r = \Phi \frac{\lambda}{hcN_L V} I_{\text{abs}} \quad (2)$$

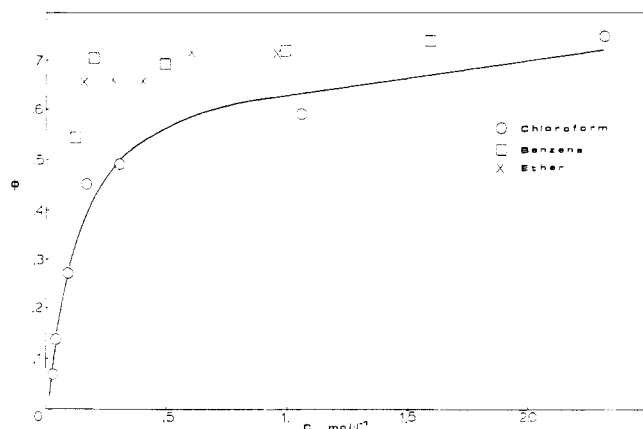


Figure 2. Dependence of quantum yield Φ on concentration of norbornadiene.

where $I_{\text{abs}} = I_0(1 - e^{-\mu c x})$, c = velocity of light, N_L = Avogadro's number, and Φ is a function of reactant concentration C , to be determined. Mass balances across the reactor and across the mixer lead to the following expression relating the concentration at the sampling point with the inherent kinetics factor Φ , the light characteristics I_0, λ, μ , and the geometrical elements of the experimental setup

$$C_1(t) - C_1(t - \tau_R) + r\tau_R = \tau_M \frac{dC_1}{dt} \quad (3)$$

Concentrations were measured via a thoroughly calibrated Perkin-Elmer, Sigma 3-B gas chromatograph with F.I.D. detector. The column used was 6 ft long, $1/4$ in. in diameter, OV-101 on Chromosorb W 80-100 mesh. The other variables were easily measured by conventional techniques, so Φ can be calculated from eq 2 and 3 with an anticipated error of $\pm 15\%$, due to propagation of errors.

Discussion of Results

Several experiments were carried out in order to find out the range of Φ values and to investigate the dependence of Φ on the system parameters. In order to have a common base for comparison, a basic set of values for the experimental parameters was established. The values for this base set were: concentration of N, 0.5 mol L^{-1} , sensitizer acetophenone with 0.02 mol L^{-1} concentration, solvent chloroform, temperature 40°C , light intensity 3.6 W . The experimental variables investigated included the following.

a. Effect of the N Concentration in the Range 0.01 – 2.6 mol L^{-1} . As seen in Figure 2, Φ was found to increase as the reactant concentration increased, with a

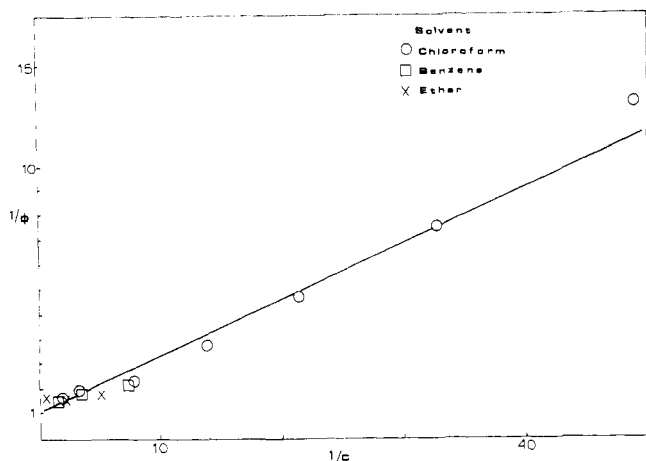


Figure 3. Testing of the relation $1/\Phi$ vs. $1/C$.

steep gradient at low concentration, which was gradually levelled as the concentration increased beyond 0.5 M. When the relation $1/\Phi$ vs. $1/C$ was tested (Figure 3), it was found that a straight line with the slope shown on the graph and an intercept of about unity could fit the data with a good correlation coefficient. Consequently, Φ takes the form

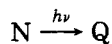
$$\Phi = \frac{k_1 C}{1 + k_2 C} \quad (4)$$

b. The Temperature of the Reaction. The range was 20–60 °C. The factor Φ was found to increase only slightly with increased temperature. No other heat effects were observed during the photochemical reaction.

c. The Nature of the Solvent. The solvents used were chloroform, benzene, and ether and the corresponding Φ values are 0.57, 0.67, 0.7 at $N = 0.5$ M. Absorption of light by the solvent was corrected for in our calculations.

It is seen from Figure 2 that chloroform yields low values for Φ , while for benzene and ether the values are the same. Perhaps this is due to the fact that chloroform was not at all an inert substance. As multiple tests showed, it reacts both with norbornadiene and quadricyclane, yielding a series of yet unidentified side products. The major side product was a substance which at the conditions of the gas chromatograph analysis (temperature of detector 200 °C, injector 150 °C, and flow rate of carrier gas (N_2) 20 mL/min) presented a retention time of 8.7 min and was ejected when the column temperature was 173 ± 3 °C (initial temperature, 35 °C; ramp rate, 35 °C/min). The formation of side products was affected by the N concentration, the sensitizer concentration, and the nature of the sensitizer.

In the case of the other solvents, no side products were formed whatever the conditions of the reaction. These results were confirmed by analogous observations when the experiments were carried out at actual sun-radiation conditions. Therefore we are led to the conclusion that chloroform should be rejected as a solvent for the photochemical reaction at either experimental or actual conditions. On the contrary, the use of benzene, cyclohexane, or ether as solvents, or pure N , is recommended, since the reaction



is really a neat reaction with a nearly 100% conversion of N to Q .

d. The Nature of the Sensitizer. The sensitizers used were acetophenone, benzophenone, and Michler's ketone, and the corresponding Φ values were 0.57, 0.38, 0.21

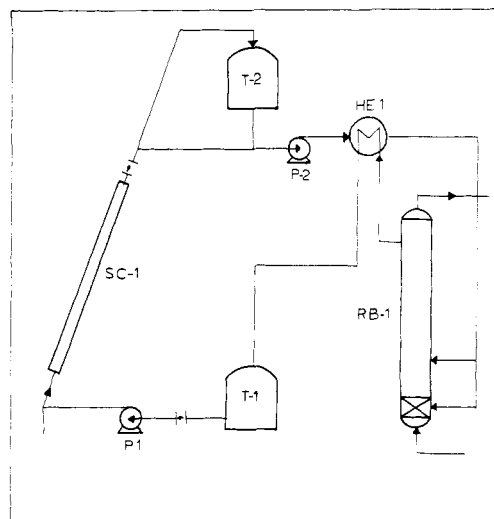


Figure 4. Flow diagram of the process (for preliminary economic evaluation).

(chloroform, $N = 0.5$ mol/L). The most efficient sensitizer was acetophenone. Very good agreement was also observed with analogous experimental results obtained from exposing the photochemical system to the sun, although in this case the intensity parameter was unsteady and uncontrolled.

Engineering Analysis

Figure 4 is a schematic flow diagram of the suggested process. It consists essentially of two sections with the associated heat-exchange, storage, and pumping equipment. It is understood, of course, that solar storage and enthalpy recovery may not necessarily be performed at the same site. However, in such a case, storage facilities should be double and fluid transportation back and forth, will be required, which will increase the energy costs.

The photochemical fluid A (norbornadiene) stored in T-1 is pumped (P-1) at slightly above atmospheric pressure through the flat-plate collector SC-1, to be converted to the energy-rich fluid B (quadricyclane), with a degree of conversion x_1 to be optimized, depending on the neatness of the photochemical reaction.

The photochemical product B either could be stored in T-2 for later use or transportation to another site, or it could be pressurized (P-2) to the suitable pressure necessary to maintain it in the liquid phase through the thermochemical section. This is a necessary requirement, because if there is a phase change of fluid B, then the size (and cost) of heat exchanger HE-1 and reactor-boiler RB-1 will be increased unduly. Heat exchanger HE-1 preheats fluid B (by exchange with the hot fluid A returning from the reactor) to the minimum temperature required to start the thermochemical back reaction (e.g., 140 °C for quadricyclane). From that point on, the fluid is further heated, by exchange and its own enthalpy of back conversion, to the maximum temperature allowed by its thermal stability (e.g., 180 °C for norbornadiene).

A very small conversion of B to A is thus obtained. The main back reaction should take place in the reactor-boiler RB-1, where energy recovery is achieved by producing low pressure steam (or hot water for that matter). RB-1 is visualized as a vertical-tube water evaporator (steam generator), where demineralized water may be fed through the vertical tubes and fluid B through the shell. The back conversion of B to A is performed essentially isothermally at a temperature, pressure, and degree of conversion optimized by the neatness of the reaction. Start-up of the reactor-boiler might present a little problem. It could

either be achieved electrically or it could be done catalytically (Jones and Ramachandran, 1976), provided a suitable catalyst is developed which starts the back-reaction, at room temperature. Thus, for start-up purposes, part of the fluid should be diverted through the catalytic section, shown in the bottom of RB-1. The heat of the catalytic reaction should take care of warming up the equipment. After the warm-up period, the fluid may be diverted from the catalytic section, to prolong the catalyst life.

The flat-plate collector is in batch operation. The end of a cycle occurs when a certain conversion has been achieved. Two main reasons lead to this specific design. One is that large residence times are required in order to have considerable conversion in the collector (of the magnitude of 100 h). The other is that the overall system efficiency is so low that a sophisticated collector design (with the anticipated minor improvement in efficiency) is not justified.

Collector Simulation. The mathematical model for the flat-plate, batch collector is in fact a rather complicated system of differential equations, as shown below.

The mass balance in dimensionless form is

$$\frac{\partial \sigma^*}{\partial \tau^2} = \frac{\partial^2 \sigma^*}{\partial \xi^2} - \phi^* A e^{-B\xi} \quad (5)$$

where σ^* , τ^* , and ξ are the dimensionless concentration, time, and plate thickness, respectively, as defined in the Nomenclature section, and ϕ^* is eq 4 in terms of σ .

$$A = \frac{L^2 \eta^* \lambda^* \mu_f^* (1 - p_g^* - a_g^*) I_0}{DhC_0N_L}$$

$B = \mu_f^* L$ and the boundary and initial conditions are $(\partial \sigma^* / \partial \xi)_{\xi=0} = (\partial \sigma^* / \partial \xi)_{\xi=1} = 0$ and $\sigma^*(\xi, 0) = 1$.

The energy balances for the top and bottom plate of the collector, respectively, are (Beckmann and Duffie, 1974)

$$(mC_p)_g \frac{dT_g}{dt} = \alpha_g^* I_0 - (5.7 + 3.8u + \epsilon_g \sigma (T_g^2 + T_\alpha^2)(T_g + T_\alpha)) + \left[\frac{K}{L} + \frac{\sigma(T_m^2 + T_g^2)(T_m + T_g)}{\frac{1}{\epsilon_g} + \frac{1}{\epsilon_m} - 1} \right] (T_m - T_g) \quad (6)$$

with $(T_g)_{t=0} = T_\alpha$

$$(mC_p)_m \frac{dT_m}{dT} = (1 - \rho_g^* - \alpha_g^*) \alpha_m^* \int_0^\infty e^{-\mu L J_\lambda} d\lambda - \left[\frac{K}{L} + \frac{\sigma(T_m^2 + T_g^2)(T_m + T_g)}{\frac{1}{\epsilon_g} + \frac{1}{\epsilon_m} - 1} \right] (T_m - T_g) - [5.7 + 3.8u + \epsilon_m \sigma (T_m^2 + T_g^2)(T_m + T_\alpha)] (T_m - T_\alpha) \quad (7)$$

with $(T_m)_{t=0} = T_\alpha$.

The temperature of the fluid T_f is obtained assuming a linear T profile between the top and bottom plates

$$T_f(x, t) = T_g(x) + x(T_m(t) - T_g(t)) \quad (8)$$

Since the photochemical reaction involves no heat, the energy balance system of differential equations can be solved, implementing a fourth-order Runge-Kutta method. The solution is inserted into the mass balance eq 5 through the experimentally determined dependence of Φ on the fluid temperature. Finally, the mass balance is solved with

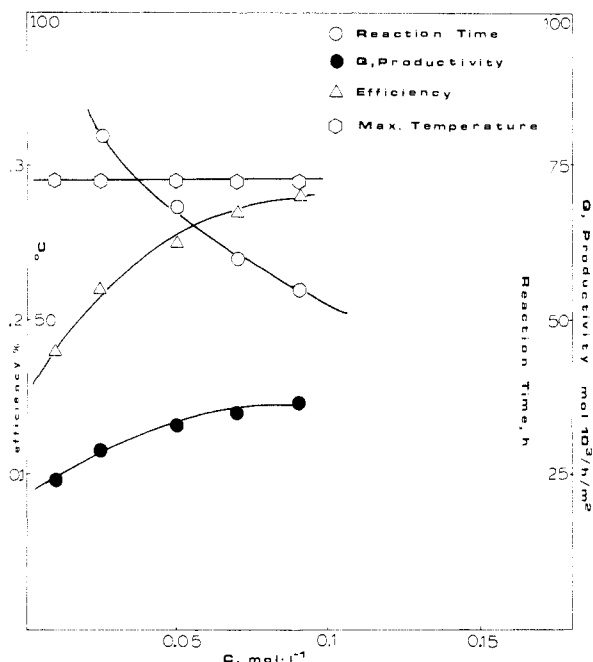


Figure 5. Dependence of collector's characteristic values on final norbornadiene concentration.

the classical Crank-Nicolson method. Numerical values of parameters used in these calculations included $\lambda^* = 3 \times 10^{-7}$ m; $\mu_f^* = 180$ m⁻¹; $\eta^* = 0.05$; $D = 3.97 \times 10^{-9}$ m² s⁻¹; $\rho_g^* = 0.02$; $\alpha_g^* = 0.06$; $\epsilon_g = 0.88$; $\epsilon_m = 0.11$; $\alpha_m^* = 0.11$; $\alpha^* = 0.94$; $K = 1.4 \times 10^{-3}$ J m⁻¹ s⁻¹ K⁻¹; $(mC_p)_g = 4520$ J m⁻² K⁻¹; $(mC_p)_m = 8600$ J m⁻² K⁻¹.

The solution of the complete set of equations yields the C and T profiles across the fluid. Consequently, several interesting quantities (such as the chemical energy stored, the overall efficiency, etc.) can be computed.

Simulation of the collector performance can be achieved by solving the system through a series of time intervals $\Delta\tau$ ($\Delta\tau$ must be conveniently small for convergence). Two cases were considered: (a) operation under constant conditions (that is λ , I_0 , T_α , u constant); this type of operation can be reproduced in the laboratory; (b) operation under randomly changing atmospheric conditions; implementation of hourly values for I_α , T_α , u (those actually measured in the year 1977 in the city of Athens were used) and the optimum collector orientation, the yearly collector performance under "real life" conditions was simulated. Both cases led to agreeing conclusions. The collector efficiency of chemical storage ranged from 0.1 to 0.5% with an average of 0.2%. This is a really low value. This is due to the values for the useful part of the total incident solar energy ($\eta^* \approx 5\%$). The efficiency is largely dependent on the N feed concentration and the desired conversion. High feed concentration and low conversion lead to increased efficiency and vice versa. The efficiency increases with increased collector thickness L (until a limit of 0.015 m), I_0 and T_α . The quadricyclane production ranged from 0.007 to 0.12 mol h⁻¹. The residence time ranged from 50 to 500 h. The fluid temperature for the year-round operation presented a maximum of 75 °C to a minimum of 2 °C. This fact secures the system from problems of elevated vapor pressure or freezing. The above are depicted in Figures 5, 6, and 7.

The Thermochemical Recovery Section. This section is more clearly shown in Figure 8. The analysis of such a system is carried out by the classical techniques of chemical engineering. The mathematical model of this section is shown below. This model is easily solved and used properly for the system integration.

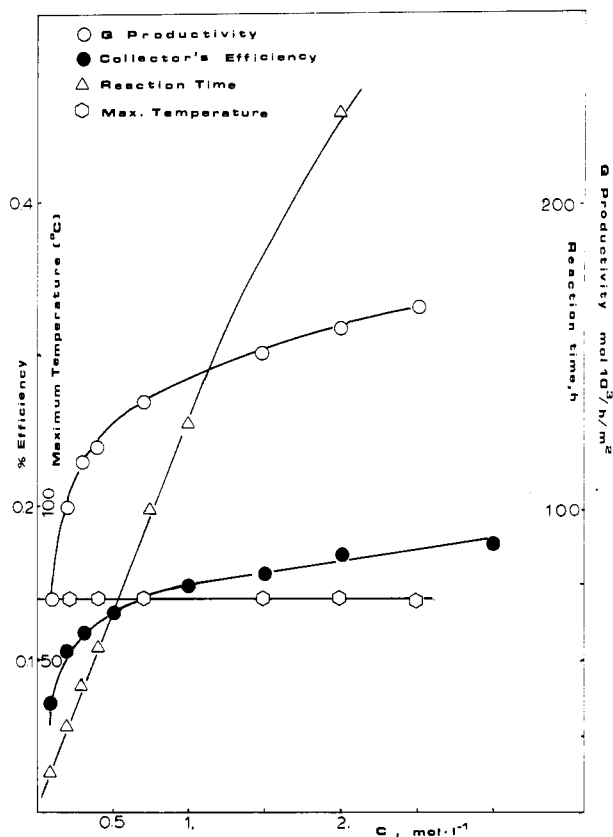


Figure 6. Dependence of collector's characteristic values on initial norbornadiene concentration.

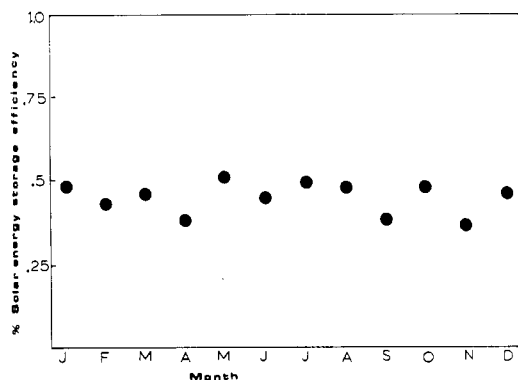


Figure 7. Dependence of collector efficiency on the month of the year (1977).

Mathematical Model for the Thermochemical Recovery Section. (Preheater-Exchanger PE-1). Mass balance for quadricyclane

$$\frac{dn_Q}{dz} = r \frac{\pi D_i^2}{4}; r = 10^{15} \exp(-19275/T) C_{i,Q} \times (1 - \zeta) \quad (9)$$

where n_Q = molar feed for quadricyclane, mol/s; ζ = conversion; and r = rate of reaction, kmol/(m³)(s) (Kakaboff et al., 1975).

Energy balance

$$\frac{dT}{dz} = \frac{1}{N_m C_{P,m}} \pi D_i U_i (T_{\vartheta_i} - T_{\vartheta_0}) + \frac{\pi D_i^2}{4} (-\Delta H_R) r; T(z=0) = T_i \quad (10)$$

N_m = total molar feed of the mixture, mol/s; $C_{P,m}$ = specific molar heat of the mixture, J mol⁻¹ K⁻¹; ΔH_R = en-

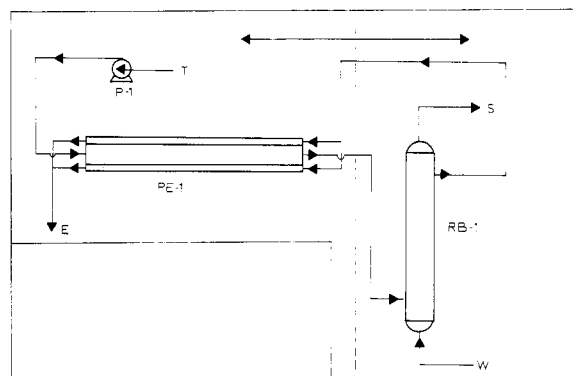


Figure 8. Flow diagram for the thermochemical-reaction section: RB-1, reactor-boiler; PE-1, exchanger-preheater; P-1, feed pump; W, water; S, steam; T, feed; E, exit.

thalpy of reaction, J/mol; U_i = overall heat transfer coefficient, W/(m)(K).

Momentum balance

$$-\frac{dP}{dz} = \frac{2f}{D_i} + \frac{J}{\pi r_b} \rho \bar{u}^2; P(z=0) = P_i \quad (11)$$

where $J = (0.7(\Delta/90^\circ)^{0.35})(0.051 + 0.19D_i/r_b)$; f = Fanning coefficient; Δ = bend angle, 180°; r_b = hydraulic radius, m; ρ = density of the fluid, kg/m³; \bar{u} = mean velocity in tubes, m s⁻¹.

Reactor-Boiler RB-1. (a) Mass Balance

$$\frac{d\zeta}{dV_R} = \frac{r}{FC_{F,Q}}; r = 10^{15} \exp(-19275/T) C_{F,Q} (1 - \zeta) \text{ kmol}/(\text{m}^3)(\text{s}) \quad (12)$$

V_R = reactor volume m³; $C_{F,Q}$ = quadricyclane feed concentration, kmol/m³; and F = feed flow rate, m³/s.

(b) Thermal Balance

$$(-\Delta H_R)(FC_{F,\alpha}) d\zeta = (UN_i \pi D_i dL_i)(T_\vartheta - T_s) \quad (13)$$

where $U = 0.03$ cal/cm² s K; N_i = number of tubes; T_s = steam temperature; and T_ϑ = temperature in tubes, where i indicates parameters inside tubes.

Sensitivity analysis of this model has shown that the most important design variables are the inlet temperature of the feed liquid, the molar flow rate of the feed, the desired final conversion, and to a lesser degree the molar ratio N:Q.

Economic Evaluation

Calculations based on the foregoing remarks lead to the unit sizes shown in Table II for a photochemical solar energy plant of 100 kW. In the same table the economics of the process are summarized.

For comparison the cost of the steam produced is evaluated. It is seen at once that this cost is heavily dependent on the number of life cycles of the system.

Figure 9 is a plot of the steam production cost vs. the number of life-cycles N . It shows that the steam produced costs from 50 ($N = \infty$) to 1000 ($N = 10$) times more than the cost of producing low-pressure steam with conventional methods.

In order to elucidate further the plant economics, break-even point analysis was performed for the two main parameters (collector efficiency and number of life-cycles). For this specific plant capacity it was found impossible for the system to achieve steam production at competitive cost, even for a 100% efficiency and an infinite number of life-cycles. For a larger capacity plant (1 MW), economic operation can be achieved for a set of values for the pair (η, N) ranging from ($\eta = 66\%$, $N = 100$) to ($\eta = 22\%$, $N = \infty$). Even for this last limiting case, economic plant op-

Table II. Summary of the Plant Design and Economics

units	size	installed cost (year 1981), \$
1. capacity: 100 kW		
2. basic design and installed cost of major equipment		
photochemical collector SC-1	116 000 m ² of surface exposed to solar radiation 2 cm thickness, [95% conversion, 0.4% efficiency, 95% Norbo in feed, 0.1% acetophenone]	2 320 000 C (\$20/m ²)
storage tanks T-1, T-2	120 m ³ of capacity each	60 000
heat exchanger HE-1	annular, i.d. 2.5 and 5 cm, length 102 m	2 500
reactor boiler	27 tubes, 4.7 m each, i.d. 1.9 cm, cell diameter 0.6 m, conversion of Q-N 95% steam production 46.1 g steam (110 psia, 175 °C)/\$	15 000
pumps	centrifugal, one medium pressure, one low pressure	4 000
total	installed cost	2 401 500
3. material cost		
volume of N required for filling the collector	2320 m ³	
cost (at \$6 per gallon):	\$7 380 000	

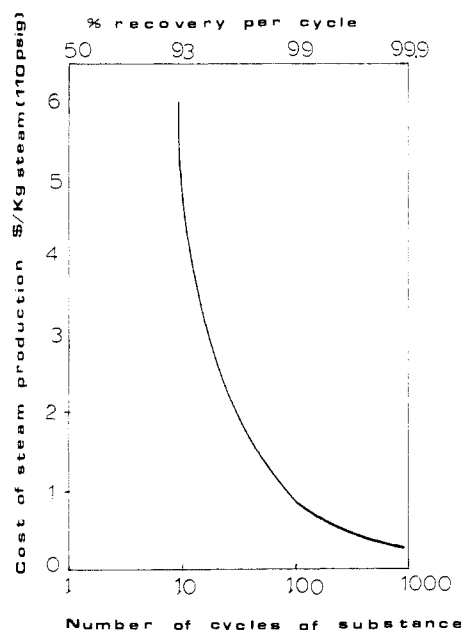


Figure 9. Dependence of the cost of steam production on the lifetime of the reacting species.

eration is impossible since there exists a limit in the collector efficiency of 12%.

Concluding Remarks

As shown above, a photochemical solar energy storage plant implementing the N/Q system, although technically feasible, is not economically justified.

Minor improvements in the collector section are possible through sophisticated collector design and strategy of operation. However, the collector efficiency is not to be significantly improved because of the inherent limitations of the low values of the efficiency terms Φ and η^* . On the other hand, improvements in the thermal recovery section, however efficient, are insignificant, since the collector represents almost 97% of the total installed cost.

Research work is carried on in order to fully examine the system characteristics in the visible spectrum. These efforts are focused on the possibility of increasing the Φ and η^* by either varying the sensitizer nature and concentration or using systems of sensitizers.

Computational work is done on the merits of combining the photochemical storage process with some other solar energy technique. In this, the photochemical storage system may be placed on a classical thermal collector system. The photochemical fluid fills one of the empty spaces between the collector covers. The two processes are complimentary since each uses a different part of the

solar spectrum. The economics of such combinations are being considered in order to judge their justification.

Acknowledgment

The authors wish to thank Shell (Hellas), S.A. for the donation of norbornadiene, and one of us (C.P.) is grateful for a Hellenic Scholarship Foundation Fellowship.

Nomenclature

a, b = empirical parameters
 A, B = parameters
 C = concentration of reactant, kmol m⁻³
 C_s = sensitizer concentration, kmol m⁻³
 C_0 = initial concentration, kmol m⁻³
 C_p = specific heat J kg⁻¹ K⁻¹
 D = diffusion coefficient m² s⁻¹
 F = flow rate, m³ s⁻¹
 h = Planck's constant
 I = solar radiation transmitted, W m⁻²
 I_{abs} = solar radiation absorbed, W m⁻²
 I_0 = incident solar radiation, W m⁻²
 $J_\lambda = I_\lambda/\lambda$ irradiation per unit wavelength, W m⁻² m⁻¹
 k = reaction rate constant, defined by eq 4
 L = collector fluid thickness, m
 m = mass of plate, kg m⁻²
 r = reaction rate, kmol m⁻³ s⁻¹
 R_1, R_2 = annular ring radii, m
 T_α = ambient air temperature, K
 T_g = top plate temperature, K
 T_m = bottom plate temperature, K
 T_f = fluid temperature, K
 t = time, s
 u = wind velocity past to plate, m s⁻¹
 V = reactant volume, m³
 x = distance along collector thickness, m
 z = longitudinal distance, m

Greek Letters

α_g^* = top plate absorptivity = 0.06
 α_m^* = bottom plate absorptivity = 0.94
 ϵ_g = top plate emmissivity = 0.88
 ϵ_m = bottom plate emmissivity = 0.11
 ζ = fractional conversion
 η^* = useful part of total incident solar energy
 λ = radiation wavelength, m
 μ_f = attenuation coefficient of fluid, m⁻¹
 ν = radiation frequency, m⁻¹
 $\xi = x/L$, dimensionless collector thickness
 ρ_g^* = top plate transmittance = 0.02
 $\sigma_g^* = C/C_0$, dimensionless reactant concentration
 σ = Boltzmann constant
 $\tau = Dt/L^2$, dimensionless time
 τ_m = residence time in mixer, s
 τ_R = residence time in reactor, s

Registry No. Norbornadiene, 121-46-0; acetophenone, 98-86-2; benzophenone, 119-61-9; Michler's ketone, 90-94-8.

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Received for review October 6, 1982

Revised manuscript received April 7, 1983

Accepted April 21, 1983

Conversion of Biomass into Chemicals with High-Temperature Wet Oxidation

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High-temperature (172–277 °C) wet oxidation of woods leads to the production of a mixture of organic acids. The organic compounds produced include formic acid, acetic acid, methanol, and a mixture of hydroxylated organic acids. In this study, the effects of oxygen pressure, temperature, the type of wood, and the addition of ferric sulfate on the yield of the organic acids were determined.

Introduction

The potential for using waste biomass as a source of fuel and chemicals to partially replace petroleum requirements has been reviewed (Goldstein, 1981). This potential can be realized only if processes that are both economical and efficient are developed for converting the biomass. In an earlier paper, our laboratory has reported some initial results of a biomass pretreatment process which uses water and high-pressure oxygen (McGinnis et al., 1983). The major reaction of biomass under relatively mild wet-oxidation conditions (120–172 °C) was solubilization of the hemicellulose and partial solubilization of the lignin. Thus, the wet-oxidation products are a liquid fraction containing dissolved hemicelluloses and lignin and a solid fraction enriched in cellulose but also containing some lignin. The wet-oxidation pretreatment not only fractionated the biomass sample, but also rendered the cellulose more susceptible for acid hydrolysis to glucose, an important result if fermentation to ethanol is the desired end-product for the biomass conversion.

At higher wet-oxidation temperatures (172–227 °C), the reaction became increasingly more oxidative and caused a considerable amount of fragmentation and oxidation of the biomass, ultimately leading to the formation of a series of organic acids plus smaller amounts of neutral organic compounds (Schaleger and Brink, 1977, 1978). Schaleger and Brink identified formic, acetic, glycolic, oxalic, levulinic, and succinic acids as the major products formed by the wet oxidation of wood. They also identified a series of neutral compounds, including glucose, mannose, xylose,

Table I. Wet-Oxidation Conditions

temperature	171–227 °C
time	30 min
oxygen pressure	240–480 psi ^a
wood	15 g
water	150 mL
reactor volume	600 mL

^a Initial oxygen pressure in the reactor at 25 °C.

galactose, arabinose, and methanol. This study was done with air at pressures at 45–100 psi and temperatures between 160 and 220 °C.

The study described here was undertaken to identify more fully the products formed by high-temperature wet oxidation and to determine how various reaction parameters, such as oxygen pressure, temperature, wood species, and the presence of metal salts, affect the yield of these products.

Experimental Materials and Methods

Three types of biomass from the southeastern United States were used; loblolly pine (*Pinus taeda* L.), black oak (*Quercus velutina* Lam.), and a sample of mixed hardwood materials obtained by whole tree chipping. Bark from the pine and oak was removed; the wood was dried and then ground to pass a 2-mm screen in a Wiley mill. The mixed hardwood material, containing approximately 15% bark and twigs, was used directly after grinding. The wet-oxidation conditions used in this study are listed in Table I.

The ground wood and water were mixed in a weight ratio of 1:10 and placed in a 600-mL reactor (Parr Model 4521). At the conclusion of the wet-oxidation reaction, the solids and liquids were separated by filtration. The solid material was air dried, weighed, and stored in an air-tight container. A small sample was removed, weighed accurately, and

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