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FORM-STABLE CRYSTALLINE POLYMER PELLETS FOR THERMAL
ENERGY STORAGE—HIGH DENSITY POLYETHYLENE INTERMEDIATE
PRODUCTS

Final Report, October 1, 1977—January 31, 1978

By
Ruth A. Botham
George L. Ball III
George H. Jenkins
Ival O. Salyer

Work Performed Under Contract No. W-7405-ENG-26

Dayton Laboratory
Monsanto Research Corporation
Dayton, Ohio

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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Work Performed by
Monsanto Research Corporation
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Under Subcontract 7398
for the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

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ABSTRACT

The primary objectives of this program were to demonstrate 1) that form-stable high density polyethylene (HDPE), which has been shown to have desirable properties as a phase-change type of thermal energy storage material, could be produced by processing in a polyethylene plant for a projected price near 26¢/lb, and 2) that the raw material, ethylene, will be available in the very long-term from alternate sources (other than petroleum and natural gas). These objectives were accomplished. Production of useful, form-stable HDPE pellets by radiation cross-linking was demonstrated. Such pellets are estimated to be obtainable at 26¢/lb, using large-volume ($\sim 10,000,000$ lb/yr) in-plant processing. Well-developed technologies exist for obtaining ethylene from coal and plant (or biomass) sources, thus assuring its long-term availability and therefore that of polyethylene.

A cost-benefit analysis of the HDPE thermal energy storage system was conducted over its 120-140°C optimum operating range which is most suited for absorption air conditioning. The HDPE is more cost effective than either rocks, ethylene glycol, or pressurized water and is even competitive with a hypothetical 5¢/lb salt-hydrate melting in this temperature range. These results applied, as appropriate, to both air and liquid transfer systems.

FOREWORD

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Project Period: October 1, 1977 - January 31, 1978

Funded Amount: \$38,500

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Acknowledgements:

The technical assistance of the following personnel in the performance of this project is acknowledged: C. F. Fritsch, R. C. Gable, and R. D. Myers.

COMMON SYMBOLS AND ABBREVIATIONS USED

TES	thermal energy storage
DSC	differential scanning calorimetry (or calorimeter)
HDPE	high density polyethylene (high crystallinity - linear)
LDPE	low density polyethylene (low crystallinity - branched)
PE	polyethylene
VTES	vinyl triethoxysilane
VTMS	vinyl trimethoxysilane
M.I.	melt index, dg/min
ΔH_f	heat of fusion, cal/g
T_M	melting temperature, °C
RT	room temperature (~23°C)
-	chemical bond
m.p.	melting point
cal	calories
g	grams
cc	cubic centimeter
phr	parts per hundred resin (weight)
°C	degrees centigrade
min	minute
<	less than
>	greater than

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1. INTRODUCTION AND BACKGROUND

In Phase 1 of a DOE-funded program on form-stable crystalline polymer pellets for thermal energy storage,¹ an efficient thermal energy storage (TES) bed material was developed that provided 48 cal/g heat of fusion at 130°C. This temperature is in the range suitable for solar absorption air conditioning applications. The output of the system was defined, and found to be acceptable, and the material was shown to be highly durable. The only barrier to its further consideration was DOE's concern over its cost and the continued availability of raw material for it from other than petroleum and natural gas feed stocks.

A price for the TES bed material, which is high density polyethylene plastic pellets processed so as to have the necessary form stability, was projected to be in the range of 25-26¢ per pound. This cost projection was based on the use of a low cost polyethylene plant intermediate, processing of this intermediate to provide form stability within the polyethylene production plant, and multi-million pound per year sales volume.

The objective of this phase of the program was to determine whether these initial cost and performance projections are valid and whether the once-through plant production of polyethylene from a lower cost intermediate can provide the same performance as that achieved in the laboratory with existing higher cost commercial products. Another objective was to determine what long-term alternate ethylene sources will be available in the future.

In this phase of the program, eight tasks were to be undertaken as follows:

1. Define specifications for the desired low-cost, high-density polyethylene (HDPE) intermediate product(s).
2. Obtain evaluation quantities, data, and price information on high density polyethylene intermediates from three prime manufacturers.
3. Process at least six of the HDPE intermediates obtained to achieve form stability.
4. Characterize the storage ability, form stability, durability, and cost of the candidates.
5. Continue melt/freeze cycling and analysis of the prime candidate silane-grafted/crosslinked HDPE defined in Phase 1 in the 60-gallon prototype TES test unit to establish long-term durability.

6. Demonstrate the storage ability of the HDPE TES system using air thermal transfer.
7. Define alternate synthesis routes to ethylene, and thereby high density polyethylene, utilizing feed stocks other than petroleum and natural gas.
8. Prepare a cost/benefit analysis of the HDPE TES system in comparison to other TES systems.

This report on the project discusses the work accomplished and results obtained on each of these tasks, and gives the conclusions reached.

2. SUMMARY AND CONCLUSIONS

The primary objectives of this program, namely, to demonstrate that 1) form-stable HDPE could be produced by in-line processing within a polyethylene manufacturing plant in the projected price range of 25-27¢/lb, and, 2) that ethylene will be available from sources other than petroleum and natural gas in the long-term, were accomplished. In addition, a cost-benefit analysis of the HDPE TES system showed that in its 120-140°C optimum operating range (which is most suited for absorption air conditioning, this storage system is at least slightly more cost effective than rocks, ethylene glycol alone, and pressurized water. It is also competitive with a hypothetical 5¢/lb salt-hydrate (no such material is known that is useful in this temperature range). These results apply both to air and liquid transfer systems, as appropriate.

A more detailed summary of the results obtained and conclusions is given on a task basis.

2.1 TASKS 1-4, DEFINING FORM-STABLE HDPE MADE FROM LOWER COST "INTERMEDIATE" PRODUCTS AND PROCESSES

The first four tasks in the project involved obtaining, characterizing, and processing low-cost HDPE "intermediates" to give form-stable products. The form-stable products were characterized and tested for durability. Then, the economics of processing by various methods were determined, and starting resin HDPE specifications were set.

It was determined that lower cost "in-line" processing of HDPE intermediate powders to give useful form-stable products via silane-grafting and crosslinking should be feasible in a typical HDPE manufacturing plant, with no major modification of the process or equipment used. The estimated selling price was projected at 34¢/lb, assuming large volume ($\geq 10,000,000$ lb/yr) production.

Alternately, radiation crosslinking was shown to be a more cost-effective method of processing the HDPE to give form-stable products, with a final estimated selling price of 26¢/lb possible (again large volumes and in-plant processing were projected). Such radiation crosslinked HDPE products were evaluated briefly in this program and found to be satisfactory in terms of initial form-stability and retention of heat of fusion (ΔH_f).

Based primarily on durability test results for the silane-grafted/ crosslinked form-stable HDPE products, specifications were set for the starting HDPE resins. These include: density ≥ 0.96 ; Melt Index (M.I.)=0.9 to 20 (g/10 min); standard anti-oxidants and stabilizers to be included; and preferred physical forms - powders for silane-grafting/crosslinking and pellets for radiation crosslinking. In essence, almost any high density polyethylene can be used.

2.2 TASKS 5 AND 6, MELT-FREEZE CYCLING OF SILANE-GRAFTED CROSS-LINKED HDPE WITH BOTH LIQUID AND AIR THERMAL TRANSFER

Melt-freeze cycling of the prime candidate silane-grafted/cross-linked HDPE in the 60-gallon prototype TES test unit was continued to a total of 632 melt-freeze cycles using ethylene glycol liquid heat transfer. No change in energy storage capacity of the pellets was found. In addition, a similar form-stable HDPE TES pellet bed material was cycled around its melting point in a small lab-scale bed using air thermal transfer. The energy storage capability of the pellets was demonstrated. There was essentially no change in ΔH_f of the pellets after 25 cycles, and the material retained its form stability.

2.3 TASKS 7 AND 8, ALTERNATE ETHYLENE SYNTHESIS ROUTES AND COST-BENEFIT ANALYSIS OF THE HDPE TES SYSTEM

Because of a concern about the long-term availability of ethylene, which is presently derived from petroleum and natural gas, a literature search was conducted to define alternate routes. The primary alternate sources identified were plants (a renewable resource) and coal. Ethylene can be obtained either from living plants that produce hydrocarbon latices, or from other plant (or biomass) products (e.g., by fermentation of sugar to ethanol and dehydration to ethylene). Ethylene production from coal, via either gasification or liquefaction, is another alternate synthesis route, and the technology is already well-developed. Thus, long-term availability of ethylene is assured.

The costs developed for a complete HDPE-TES system, including all hardware and labor, operating in its optimum temperature range of 120-140°C, were determined to be 0.94¢/BTU for a liquid thermal transfer system (with ethylene glycol) and 0.79¢/BTU for air thermal transfer. These costs are about half that for ethylene glycol alone, slightly lower than that for rocks or pressurized water, and competitive with a hypothetical 5¢/lb salt-hydrate that would melt in this temperature range, for liquid thermal transfer systems.

Similar relative costs were obtained for air thermal transfer compared with rocks or the "salt-hydrate". The overall favorable cost comparisons, in spite of higher initial materials costs, resulted primarily from the larger volumes (and hence, larger, more expensive storage tanks) required for the other storage media, which utilize sensible heat only, and the need for expensive heat exchangers with salt-hydrate type systems which also utilize heat of fusion. Thus, both the importance of the heat of fusion contribution and the pellet bed concept where the HDPE material serves as its own heat exchanger were demonstrated.

Other economic and conservation benefits of this energy storage system were also determined. The use of this HDPE-TES system in 1 million homes in the USA could result in a energy savings equivalent to 56,000 barrels of crude oil/per use cycle. A conservative estimate of 150 days/year use and a 20-year lifetime, would place the savings in crude oil (or its equivalent) at 168 million barrels. The use of this HDPE-TES material for electric load leveling from a public utility could reduce the requirement for additional electric generating facilities, thus saving on capital expenditures.

Overall, the potential savings in energy and capital expenses that could be realized from its use, combined with the demonstrated advantages and favorable economics of the HDPE-TES system, should act as stimuli for its implementation in the near future. This is particularly true since relatively little is needed in the way of further development work prior to actual introduction in the market place.

3. RESULTS AND DISCUSSION

3.1 TASKS 1-4, FORM-STABLE HDPE "INTERMEDIATE" PRODUCTS

The first four tasks of project are interrelated and hence will be considered together. This work will be discussed in the following order: (1) obtaining and characterizing HDPE "intermediate" samples; (2) processing of the HDPE "intermediates" to give form-stable products; (3) characterization and durability testing of the form-stable products; and (4) defining costs, specifications, and the economics of processing by the various methods used.

3.1.1 HDPE "Intermediate" Products

At the beginning of this project, four manufacturers of HDPE resins (Monsanto, Phillips, DuPont and Union Carbide) were contacted for samples and data on cost and physical properties for their "intermediate" HDPE products. Three difficulties were encountered. First, the length of the project was too short to allow time for shipping, processing, and complete characterization of the various samples. Second, the PE manufacturers do not make all of their various HDPE "products" continuously, so they are available only at certain times. Third, the "intermediates" are not normally isolated but are contained in a closed system and carried through to the final form. Obtaining "intermediate" PE samples thus involved interruption of continuous processing lines which operate at a rate of thousands of pounds per hour and could only be done at an unspecified time.

Thus, only one HDPE intermediate sample could be obtained from Monsanto; it was the only one being produced at the time that would meet the density requirements. Only two of the three Phillip's Petroleum Company intermediate samples promised were received in time for inclusion in the test program. Du Pont could not supply any intermediate HDPE powder samples. Instead, they referred us to companies which sell their "second" grade materials at a reduced price [generally, these "seconds" do not meet commercial melt index (M.I.) specifications.] A HDPE sample was never received from Union Carbide.

Table 1 contains pertinent physical property data on these HDPE "intermediates" and "seconds" which were promised (whether or not received). The one initial specification was density (≥ 0.96). Melt index was intentionally varied widely, in order to determine its effect on properties of the final crosslinked products. Cost data are given in section 3.5, where the overall processing economics are discussed. All of the intermediate products were

Table 1. HDPE INTERMEDIATE OR "OFF-SPEC" PRODUCT INFORMATION

<u>Manufacturer (or supplier)</u>	<u>HDPE Products Requested</u>			<u>Product Physical Properties</u>			
	<u>Product Designation</u>	<u>Physical^(a) Form</u>	<u>Sample Received</u>	<u>Melt Index^(b) (M.I.) (g/10 min)</u>	<u>Density^(b) (g/cc)</u>	<u>DSC Characterization^(c)</u>	
						<u>T_m^(d) (°C)</u>	<u>ΔH_f^(d) (cal/g)</u>
1. Monsanto Company Texas City, Texas	PE Plastic Powder Lot 55071 T271-3	powder	yes	12	~0.96	128	40.3
2. E. I. Du Pont Co. Orange, Texas	<u>Supplier:</u>						
a. Hemisphere Polymer and Chemical Co. Worcester, Mass.	Alathon PE Lot 755697 MD 801	pellets	yes	0.93	0.959	132	44.6
b. Rapid Industries Jersey City, N.J.	Alathon 7040 PE Lot 656015	pellets	yes	6.1 ^(a)	~0.96	132	45.2
3. Phillips Petroleum Co. Pasadena, Texas	Marlex:						
	- EHM 6006	powder	yes	0.6	0.96	133	47.0
	- TR-885	powder	yes	30	0.96	131	49.3
	- EMN 6030	powder	not until Jan. 1978	3	0.96	-	-
4. Union Carbide Corp. Seadrift, Texas	Extrusion grade (vapor phase process)		no	-	~0.96	-	-

(a) Powders = intermediate products; Pellets = "off-spec" products.

(b) Manufacturer's Data

(c) MRC Data

(d) T_m = crystalline melting point and ΔH_f = heat of fusion. Values are average of 3 separate DSC samples (3 melting cycles each). DSC Conditions -10°C/min heating and cooling rate, range 8, chart speed 20 mm/min., indium standard for calibration.

"powder" samples (without the standard additives, such as UV stabilizers or anti-static agents), while the "seconds" or "off-spec" products were finished pellets with additives. Some processing differences were noted between powder and pellets, as will be described in section 3.1.2. The HDPE samples were characterized by differential scanning calorimetry (DSC) as described previously,¹ and all had heat of fusion (ΔH_f) values ≥ 40 cal/g before processing, the lowest being Monsanto's PE (40.3 cal/g), and the highest being Phillip's TR-885 (49.3 cal/g).

3.1.2 Processing of HDPE "Intermediates" Into Form-Stable Products

3.1.2.1 Silane-Grafting/Crosslinking Procedures

Processing of the HDPE intermediate and "off-spec" products, to form-stable products was carried out primarily via silane-grafting and crosslinking. The same ingredients and processing conditions were employed as had been used in preparing the 250 pounds of silane-grafted/crosslinked TES material in Phase 1.¹ This procedure is summarized as follows:

1. A charge of 2000 g of Alathon 7040 HDPE (Du Pont) pellets was added to a large Banbury mixer and fluxed 4 to 5 minutes at a temperature above RT (no steam). A charge of 120 g (6 phr) vinyl triethoxy silane (Union Carbide A-151) containing 4 g (0.2 phr) benzoyl peroxide was added and 5 min of mixing with steam on (120 psi) begun. At the end of this time, cooling water was turned on and the ~4 lb silane-grafted PE cake was removed from the Banbury (after 2 min cooling time).
2. The grafted PE cake was next cold pressed into round, flat discs which could readily be cut into strips via a bandsaw, and then granulated into flakes or pieces suited for extrusion.
3. The silane-grafted flakes were next co-extruded in a 95/5 (w/w) ratio with a catalyst batch (consisting of 100 parts Alathon 7040, 1 phr dibutyltin dilaurate and 0.15 phr benzoyl peroxide prepared via mixing on a hot mill roll, and granulated into flakes) using a 1 inch extruder (2 passes, all heated zones at 165°C) (330°F) and chopped into pellets.
4. These silane-grafted HDPE pellets were next crosslinked by heating in 88°C water for 48 hours, removed, rinsed thoroughly with H₂O, and air-dried.

Any difference in the silane-grafting/crosslinking processing conditions and/or amounts of materials used (from those employed in the 250 pound batch preparation) are noted in Table 2.

Table 2. PROCESSING OF HDPE INTERMEDIATES VIA SILANE-GRAFTING/CROSSLINKING TO ACHIEVE FORM-STABILITY

HDPE Starting Material		VTES ^(a) Conc. (phr)	Silane-Grafting/Crosslinking Processing Variations Used			Processed Sample Designation ^(c)
Manufacturer and Designation (Supplier)	Physical Form		VTES Blending Method	Extrusion Temperature (°F)	Crosslinked ^(b)	
Monsanto Company Lot 55071, T271-3	powder	6	Dry blend before addition to Banbury mixer	350	no yes	1A 1B
		6	All components blended in small (1 lb) Banbury mixer, then extruded	350	no yes	2A 2B
		3	All components blend- ed in large (5 lb) Banbury mixer, then extruded	350	no yes	3A 3B
Du Pont Alathon PE Lot 755697, MD 801 (Hemisphere Company)	pellets	6	Add to molten PE in Banbury mixer	380	no yes	4A 4B
Du Pont Alathon 7040 PE Lot 656015 (Rapid Ind.)	pellets	6	Add to molten PE in Banbury mixer	340	no yes	5A 5B
Phillip's Marlex EHM-6006	powder	6	Dry blend before addition to Banbury mixer	420	no yes	6A 6B
Phillip's Marlex TR-885	powder	6	Dry blend before addition to Banbury mixer	345	no yes	7A 7B

(a) VTES - Vinyltriethoxy silane.

(b) Conditions for crosslinking - 24 hr/boiling H₂O.

(c) Original Designations - NBP-2C7838 (1-4), and 207839 (1-3).

One processing difference, in the case of the HDPE powder samples, was that the silane/peroxide mixture was added directly to the powder before fluxing in the Banbury intensive mixer. This, in contrast to adding the silane to the molten PE in the Banbury, resulted in better mixing and less silane loss via evaporation during processing. This improvement was possible because the high surface area powders readily absorbed the liquid silane, whereas the PE pellets did not.

Some slight variations also existed in extrusion conditions. The lower melt index (M.I.) samples were extruded at higher temperatures than the higher M.I. (lower molecular weight) samples. Only one sample, Phillip's TR-885, presented even any minor processing problems. It was sufficiently high in M.I. (and hence low in melt viscosity) so that extrusion was slightly more difficult with it than with the other PE samples.

A sample of Monsanto's HDPE was processed by adding all components into the Banbury mixer [instead of adding the dibutyltin dilaurate (DBTDL) catalyst to a molten PE master batch separately, then coextruding]. This was done to more closely simulate possible processing conditions in a HDPE plant. Form-stability test results suggested that the vinyltriethoxy silane (VTES) concentration could be reduced using this processing method, with obvious cost benefits. Therefore, a sample of the Monsanto HDPE powder was processed with a greatly reduced concentration of VTES (3 phr versus 6 phr), again by adding all components to the Banbury mixer. As will be discussed in section 3.1.3, form-stable pellets were produced.

An attempt was made to crosslink a portion of this last Monsanto silane-grafted HDPE sample in a hot water bath immediately after it emerged from the extruder (to simulate plant conditions). However, with the equipment used, the water temperature was too low (~ 60 - 80°C) and the dwell time in the bath too short (~ 6 - 8 seconds) to adequately duplicate "plant" conditions (where the molten PE is extruded into $\sim 90^{\circ}\text{C}$ water with a dwell time of 30-60 seconds). Therefore, the rest of this sample was crosslinked for 24 hours in boiling H_2O (as were the others) to provide for a direct comparison of properties. In smaller "beaker scale" experiments, these same silane-grafted pellets could be crosslinked to achieve form-stability after only 1-5 min. in $\sim 100^{\circ}\text{C}$ water, when the pellets themselves were first heated to $\sim 110^{\circ}\text{C}$. This indicated that a short time/high temperature exposure available with large-scale processing would provide the necessary crosslinking.

3.1.2.2 Radiation Crosslinking

Radiation crosslinking was examined on one HDPE sample. The radiation crosslinking was done by Radiation Dynamics, Inc.,

Melville, Long Island, New York. Four different dosage levels were used, from 4.5 to 18 megarads, directly on HDPE pellets. The HDPE sample processed was the Alathon PE (0.93 M.I.) obtained from Hemisphere Company. The primary reason for examining the radiation crosslinking of PE pellets was the potential near and long-term cost advantages of this processing method, as will be discussed in section 3.1.5. It was not expected to offer any significant advantages in improvement of properties over the chemical crosslinking methods used previously.

3.1.3 Characterization and Stability Testing of the Crosslinked HDPE Products

All of the silane-grafted/crosslinked HDPE products (and, for comparison, some of the corresponding silane-grafted but uncrosslinked materials) were characterized in at least two ways: (1) thermal form-stability in air was observed via melting of multiple, touching pellets on a Fisher-Johns melting point apparatus; and (2) the heats of fusion and crystalline melting temperatures were determined using differential scanning calorimetry. Also, some of the crosslinked products were tested for gel content, to determine the extent of crosslinking. Details of the testing apparatus and procedures were given in the Phase 1 final report¹ and will not be repeated here.

Some of the better crosslinked samples were selected for additional stability and durability testing. This testing consisted of (1) melt-freeze cycling of ~25 g of the polymer pellets in ~75 ml of ethylene glycol (Prestone II brand anti-freeze) through 50 melt-freeze cycles, and (2) maintaining another 25 g of the pellets in the melt in ~200 ml of refluxing ethylene glycol for approximately one month. While these were not very long-term tests, compared to those undertaken in Phase 1 of this program, this was the best exposure which could be obtained within the time allotted for this phase.

Characterization of the radiation crosslinked HDPE's will be considered separately, after discussion of the silane-grafted/crosslinked HDPE's. Very little stability testing could be carried out on these samples because they were available for test only late in the program.

3.1.3.1 Form-Stability and Thermal Properties of Silane-Grafted and Crosslinked HDPE Products

The form-stability and thermal properties data obtained on the silane-grafted (but not crosslinked) HDPE products are summarized in Table 3, and the same property data, plus gel contents, on the silane-grafted, crosslinked PDPE products are given in Table 4.

Table 3. FORM-STABILITY AND THERMAL PROPERTIES OF THE SILANE-GRAFTED HDPE INTERMEDIATE PRODUCTS

Starting HDPE Resin		Sample Designation	Thermal Form-Stability*		Thermal Fusion Properties**		
Designation	M.I. (g/10 min)		Observations	Rating	T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained (%)
Monsanto Lot 55071, T271-3	12	1A	Pellets flatten out and flow together on melting, adhere tightly.	poor	128	36.1	90
		2A	Slight flattening of pellets on melting and slight adhesion in melt, but break apart readily.	fair	-	-	-
		3A	Slight flattening of pellets on melting and slight adhesion in melt, but break apart readily.	fair	-	-	-
Du Pont Co. Alathon PE Lot 755697, MD 801	0.93	4A	Pellets Flatten out on melting and stick slightly but can break apart.	fair	132	42.1	94
Du Pont Co. Alathon HDPE Lot 656015	6	5A	Pellets flow and flatten out as they melt; adhere firmly in melt.	poor	-	-	-
Phillips Petroleum Co. Marlex EHM-6006	0.6	6A	Only slight change in pellet shape on melting and very slight adhesion.	good	-	-	-
Phillips Petroleum Co. Marlex TR-885	30	7A	Pellets flow on melting - adhere into one mass after melting.	very poor	-	-	-

*Form-Stability: As determined by heating touching pellets (in air) to 200°C on Fisher-John's melting point apparatus.

**DSC Conditions: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min., indium standard.
T_M = crystalline melting point, ΔH_f = heat of fusion. % ΔH_f retained - compared to ΔH_f of starting HDPE (see Table 1).

Table 4. FORM-STABILITY AND THERMAL PROPERTIES OF THE SILANE-GRAFTED AND CROSSLINKED HDPE INTERMEDIATE PRODUCTS

Starting HDPE Resin			Thermal Fusion Properties**					
Designation	M.I. (g/10 min)	Sample Designation	Thermal Form-Stability*		T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained (%)	Gel [®] Content (%)
			Observations	Rating				
Monsanto Co. Lot 55071, T271-3	12	1B	Pellets retain shape on melt- ing and do not adhere.	very good	127	37.5	93	58
		2B	No flow on melting and no tendency to self-adhesion even in melt.	excellent	128	37.5	93	
		3B	No flow on melting and no tendency to self-adhesion even in melt.	excellent	128	38.2	95	
Du Pont Co. Alathon PE Lot 755697, MD E01	0.93	4B	No flow at all on melting and no tendency to self- adhere in melt.	excellent	133	42.2	95	56
Du Pont Co. Alathon 7040 PE Lot 556015	6	5B	Pellets do not flow on melting and only have slight tendency to adhere in melt - break apart readily.	good	133	44.7	99	
Phillips Petroleum Co. Marlex EHM-6C06	0.6	6B	No flow at all on melting and no self-adhesion even in melt.	excellent	130	41.5	88	70
Phillips Petroleum Co. Marlex TR-885	30	7B	Flatten only slightly on melting; stick slightly in melt, but break apart readily.	good	133	47.4	96	33

*Form-Stability: As determined by heating touching pellets (in air) to 200°C on Fisher-John's melting point apparatus.

**DSC Conditions: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min., indium standard.
 T_M = crystalline melting point, ΔH_f = heat of fusion. Values are average of three separate DSC samples (3 melting cycles each). % ΔH_f retained - compared to ΔH_f of starting HDPE (see Table 1).

[®]Gel Content: Average of 3 samples extracted 16 hr in refluxing ethyl benzene.

The form-stability of the silane-grafted and crosslinked HDPE's ranged from "good" to "excellent" in all cases. In comparison, and as expected, the form-stability of the same silane-grafted (but not crosslinked) samples, shown in Table 3, was generally "very poor" to "fair". The primary reason for comparing this form-stability with the grafted, rather than the starting, HDPE's was that the HDPE "intermediates" were powders, not pellet samples, and hence would not be tested in this form.

Slight differences in the form-stability of the silane-grafted (not crosslinked) HDPE samples were observed, depending on initial melt index of the HDPE. The high melt index (lower molecular weight) sample pellets flowed together into one mass on melting, whereas the lowest M.I. samples retained some outline of the individual pellets. It was not unexpected then that there would be some slight differences in form-stability observed among the HDPE samples after crosslinking, also.

However, with the silane-grafted/crosslinked HDPE pellet samples, any relationship between M.I. and form-stability was not as obvious, in this initial test. It was important that even the highest M.I. material (Phillip's TR-885, M.I. 30) had good form-stability, after complete processing. Also, excellent form-stability was obtained with only 3 phr vinyl-triethoxy silane (VTES), versus 6 phr for the others, when all components were added and compounded in the Banbury mixer at one time. This is of particular significance, since both process simplification and reduction of VTES concentration are permitted.

The heat of fusion retained (after crosslinking) of the silane-grafted/crosslinked polyethylenes differed only slightly, with the melt index of the starting HDPE's. This is shown graphically in Figure 1, where little change in ΔH_f occurred between M.I. 0.6 and 30, i.e., a ~50-fold increase.

This lack of effect with the silane-grafting/crosslinking process is in contrast to results obtained in Phase 1,¹ with peroxide-crosslinked HDPE samples, where the percent ΔH_f retained was considerably lower for the lower melt index HDPE's. It may reflect the difference in the type of crosslink bond formed, i.e., -C-C- for peroxide crosslinked, versus -Si-O-Si- for the silane-grafted HDPE's.

The highest actual ΔH_f value obtained with any of the HDPE's was 47 cal/g for the Phillip's TR-885, while the lowest was 38 cal/g for the Monsanto HDPE. This was simply a reflection of the differences in starting ΔH_f values, since the percent ΔH_f retained was about the same for both. Furthermore, it is

Figure 1. Melt Index vs. % ΔH_f retained for form-stable silane-grafted and crosslinked HDPE products, illustrating the independence of heat of fusion retained on molecular weight.

significant that the HDPE grafted with only 3 phr VTES also exhibited slightly higher percent ΔH_f retained (95%). It is expected that similar reductions in VTES concentration could be made with the other HDPE's (using the same processing conditions) with the same favorable results.

The gel contents of these silane-grafted and crosslinked HDPE samples, given in Table 4, directly reflect the level of crosslinking achieved (i.e., the higher the gel content, the greater the degree of crosslinking) and vary inversely with sample MI (or directly with molecular weight). This is illustrated in Figure 2. That this should be the case is not surprising, even though equivalent amounts of silane were used for grafting of all HDPE samples. More crosslinks would be required for a lower molecular weight polymer (which has presumably many more "short" chains) than for the higher molecular weight (with longer polymer chains) HDPE, to render the same weight fraction of each insoluble.

3.1.3.2 Stability/Durability Testing of Silane-Grafted Crosslinked HDPE Products

Four of the better crosslinked HDPE products were selected for stability/durability testing. Results are given in Table 5. Some differences in form-stability in these stability and durability test results were observed among these samples, which may be related in part to melt index of the starting resin and/or to the level of crosslinking attained (as indicated by the gel contents in Table 4).

On the melt-freeze cycling test (through 50 cycles) in ethylene glycol, ~93-97% of the initial ΔH_f was retained (not a significant decrease) for all of the samples. The only pellets showing any tendency to adhere were those made from Phillip's TR-885, the highest M.I. sample (with the lowest level of crosslinking). Since this was a very limited test, it may not be as indicative of HDPE crosslinked sample stability as that of keeping the HDPE pellets in the melt for ~1 month (810 hours) in refluxing ethylene glycol.

The latter test, which was certainly a more severe one, produced a wider variation in results among the four crosslinked HDPE samples tested. Clearly, the poorest sample is that prepared from Phillip's TR-885, which had a melt index of 30 (initially), and the lowest degree of crosslinking (% gel content) in the final product. It had the greatest reduction in ΔH_f (less than 90% retained) and was fused into large pieces on cooling from the melt. There is virtually no distinction among the other three samples tested; the Monsanto HDPE, had the least inter-particle adhesion and retained 94% of its initial ΔH_f value,

Figure 2. Melt Index vs. Gel Content (%) for silane-grafted/crosslinked HDPE products, illustrating the dependence of degree of cross-linking achieved on polymer molecular weight.

Table 5. EFFECT OF THERMAL CYCLING AND EXPOSURE TO ELEVATED TEMPERATURES ON FORM-STABILITY
AND HEAT OF FUSION RETENTION OF SILANE-GRAFTED/CROSSLINKED HDPE PRODUCTS

Sample Designation	Starting Resin M.I. (g/10 min.)	Exposure Conditions*		Form-Stability After Exposure		Thermal Fusion Properties**		
		Melt-Freeze ^(a) Cycles, No.	Time in Melt ^(b) (continuous), hr	Pellet Appearance at Conclusion of Test	Rating	T _M (°C)	ΔH _f (cal/g)	ΔH _f Retained (%)
2B	12	50	-	No adhesion of pellets - very slight yellowing of some pellets.	excellent	128	35.3	94
		-	810	Very little pellet adhesion - break apart readily.	very good	127	35.3	94
4B	0.93	50	-	No adhesion of the pellets, very slight yellow tinge.	excellent	133	41.1	97
		-	810	Some pellet adhesion, but break apart; slight discoloring of pellets.	good	131	40.0	95
6B	0.6	50	-	No adhesion, pellets white.	excellent	131	38.5	93
		-	810	Some adhesion, but pellets break apart.	good	130	39.8	96
7B	30	50	-	Slight adhesion of some pellets but break apart; white.	good	133	46.0	97
		-	810	Considerable adhesion, pellets fused to large pieces.	poor	113	41.1	87

*Ethylene glycol (Prestone II anti-freeze) used as liquid heat transfer medium in both tests:

(a) 25 g pellets in 75 ml ethylene glycol cycled around 130°C melting point;

(b) 25 g pellets kept molten in 200 ml refluxing ethylene glycol.

**DSC Conditions: 10°C/min. heating and cooling rate, range 8, chart speed 20 mm/min., indium standard; T_M - crystalline melting point; ΔH_f - heat of fusion (one or two DSC samples, 3 melting cycles each); % ΔH_f retained - compared to initial ΔH_f of crosslinked HDPE (see Table 4).

while the Phillip's Marlex 6006 pellets had slightly more adhesion but retained ~96% of the initial ΔH_f . Some of these ΔH_f changes are within expected normal DSC sample variation limits.

A slight yellowing of some pellets was observed, which may in part have been due to unintended overheating. However, the HDPE intermediate starting resins did not contain the usual PE antioxidants and stabilizers that are normally added, and there was some contact of the pellet surfaces with air in these tests. Thus, it would appear that inclusion of the usual HDPE antioxidants in a PE-TES material would be beneficial, and is recommended, even if there is little or no air contact in the system.

3.1.3.3 Characterization of Radiation Crosslinked HDPE Products

The radiation crosslinked HDPE samples were obtained relatively late in the program and only limited testing of them was possible. They were characterized for form-stability and ΔH_f retention (by DSC), and one sample was cycled 30 times around its melting point in ethylene glycol and then retested. Results are given in Table 6 and illustrated graphically in Figure 3.

These results that while improved form-stability was achieved with a dosage rate of only 4.5 megarads (MR), 9 megarads or greater is needed to give really good form-stability. At this point, the percent ΔH_f retained is 88% of the original ΔH_f value. As shown in Figure 3, doubling the dosage rate again, to 18 megarads, produced only a relatively small further reduction in percent ΔH_f retained. Thus, while radiation crosslinking results in a slightly lower percent ΔH_f retained, than does the silane-grafting/crosslinking method (see Table 4) at a level where adequate form-stability is achieved, the percent ΔH_f retained was still higher than was the case with peroxide crosslinking methods (see Phase 1 final report¹) when good form-stability was obtained. This may be due to the fact that radiation crosslinking is limited mainly to the polymer's amorphous regions, since there is no melting of the PE during the process.

There is a very slight yellowing of the pellets with increasing radiation dosage. For this reason, as well as in the interest of retaining maximum ΔH_f and keeping processing costs low, it probably is desirable to use the lowest possible radiation dosage level consistent with achieving good form-stability. It would appear that a dosage level of 9-10 megarads should be adequate, and is recommended as the maximum level to be used with this HDPE resin. Cycling of the sample exposed to 13.5 megarads 30 times around its melting point in ethylene glycol

Table 6. CHARACTERIZATION OF RADIATION CROSSLINKED ALATHON HDPE (0.93 M.I.) PELLETS

Radiation Dosage Megarads	Appearance of Irradiated Pellets	Thermal Fusion Properties (DSC)**				
		Form-Stability in Air*		T_M (°C)	ΔH_f (cal/g)	ΔH_f Retained (%)
		Observations	Rating			
none	white	Pellets "flatten", soften and adhere in the melt - can't readily break them apart when cooled.	fair	132	44.6	-
4.5	white	Pellets retain shape - little "flattening" - adhere slightly in melt, but break apart when cooled.	good	131	41.8	94
9.0	very faint yellow	No change in pellet shape as they melt and no tendency to self-adhere in melt (do so very slightly on cooling).	very good	130	39.3	88
13.5	faint yellow tinge	Pellets very firm in melt - no tendency to self-adhere at all in melt or as cooled.	excellent	129	38.2	86
		Cycled 30 times around m.p. in ethylene glycol - no adhesior..	excellent	129	36.1	95
18	definite yellow tinge	Pellets very firm in melt and have only a very slight tendency to self-adhere in melt.	very good to excellent	130	37.5	84

*As determined by heating touching pellets to 200°C on Fisher-John's m.p. apparatus.

** T_M - crystalline melting point; ΔH_f - heat of fusion; values for irradiated PE samples are averages of 2 separate DSC samples (3 melting cycles each). % ΔH_f -retained-compared to unirradiated Alathon PE resin, except for sample cycled 30X around m.p. (compared to ΔH_f before cycling).

DSC Conditions: 10°C/min heating and cooling rate, range 8, chart speed 20 mm/min., indium calibration standard.

Figure 3. Percent ΔH_f retained as a function of radiation dosage used in crosslinking of HDPE pellets by radiation.

produced no change in pellet appearance and no interparticle adhesion. The ΔH_f value declined slightly (to 95% of the original) but, again, this is close to the normal variation range expected from one DSC sample to another.

Overall then, radiation crosslinking of HDPE pellets appears to have certain advantages. It can be carried out on "finished" PE pellets, without requiring any remelting of them. While ΔH_f is reduced somewhat more than by the silane-grafting/crosslinking process, it is less so than by peroxide-crosslinking for comparable form-stability. The economics also appear favorable, as will be discussed in section 3.5. The work done in this project on radiation crosslinking was limited, however. It is recommended that some additional work should be undertaken, particularly in terms of studying varying M.I.'s of the starting PE and conducting more extensive stability/durability testing, before any process "scale-up" is considered.

3.1.4 Specifications for Starting HDPE Resins

Based on the results obtained in testing of these crosslinked HDPE samples (particularly the durability and stability testing) the following specifications can be set that should be met by any HDPE to be used for crosslinking to a form-stable HDPE pellet bed material:

1. Density Range ≥ 0.96 to < 1.0 (g/cc)

This density range is required to insure maximum crystallinity and a high heat of fusion value of the starting HDPE resin. This is essential since any crosslinking process will lower the heat of fusion to at least a slight extent, reducing energy storage ability. Practically, HDPE's with density ≥ 0.98 are not obtainable.

2. Melt Index Range - 0.9 to ~ 20 g/10 min (Preferred Range - 3 to 15 g/10 min)

a. Silane-Grafting/Crosslinking Process

This M.I. is recommended to maximize form-stability and ΔH_f retention on silane-grafting and crosslinking. A low (~ 0.6) M.I. HDPE sample processed to achieve form-stability via silane-grafting/crosslinking had a low percent ΔH_f retained while a high M.I. (30) HDPE sample had poor durability and form-stability (at the same level of grafting).

b. Radiation Crosslinking

The optimum M.I. levels suited for adiation crosslinking are expected to be similar, but should be determined. A 0.9 M.I. sample was processed by radiation crosslinking to give satisfactory form-stability.

3. Additives - Standard HDPE Antioxidants and Stabilizers

They are required to prevent any degradation from unexpected overheating (and particularly so, if there is any air contact in the TES system).

4. Physical Form

a. Silane-Grafting/Crosslinking

For this procedure, HDPE powder is preferred over pellets and would be the material normally used if the silane-grafting/crosslinking is conducted as an integral part of the HDPE manufacturing process.

b. Radiation crosslinking

The use of pellets would be preferred for this procedure, since no remelting to pelletize is then required after the crosslinking procedure.

3.1.5 Projected Costs of Crosslinked HDPE Products

The costs of the final crosslinked HDPE products will depend on all of the following:

- 1) ethylene cost and availability and the method used for high density polyethylene production;
- 2) The crosslinking process used (silane-grafting/crosslinking, peroxide crosslinking, or radiation crosslinking);
- 3) whether the process is carried out "in line" with HDPE production and pelletizing operations, or separately.

Each of these factors will be discussed, some in combination with one another.

3.1.5.1 Ethylene Costs and Availability

Ethylene is currently being produced at a rate of 23 billion pounds/year.² Prices are depressed due to excess supply, and this situation is expected to continue for the next several years, as shown in Figure 4, since a number of new ethylene

Figure 4. Projected U.S. ethylene supply /demand through 1981.
(Chemical Week, Sept. 14, 1977, p. 37)

units are being brought onstream during that time.² It has been projected that ethylene prices will remain relatively stable over the next few years, rising no more than to 14-15¢/lb by 1980 and 16-18¢/lb by 1982² (i.e., not more than would be expected with inflation rates of ≥6%/year). Thus, availability of ethylene in the near term is assured, and costs should remain relatively constant in terms of 1977-78 dollars.

The long-term ethylene availability (when petroleum and natural gas resources become more scarce) is considered in section 3.4. Ethylene availability appears assured, but sources may be different and no price projections can be made at this time. Presumably though, any increase will not exceed that of other, similarly energy-related, raw materials costs.

3.1.5.2 High Density Polyethylene Production

In 1976 about 9 billion pounds of polyethylene were sold in the U.S.³ Of this about 35% (about 3+ billion pounds) was high density polyethylene. With the excess supply of ethylene available, additional high volume uses for polyethylene are considered desirable by manufacturers. Widespread usage of HDPE as a TES material, with an estimated requirement of 3000 pounds per house in order to provide about one third million BTU storage capacity, would thus be both feasible and highly desirable as an outlet for excess ethylene available. If one million houses in the U.S.A. were equipped with TES units of this size, the HDPE requirement would be 3 billion pounds (nearly equivalent to present production). While it is not anticipated that a sudden demand for HDPE of this magnitude will occur, nevertheless, volumes involved could be substantial.

HDPE is manufactured by liquid or vapor phase processes at low pressures and moderate temperature. There are three types of catalyst systems used: the Ziegler-Natta catalyst system, the titanium tri- or tetrachloride with alkyl aluminum; the Phillips Petroleum catalyst system of chromium oxide on silica or silica alumina; and the Amoco system of molybdena on aluminum with sodium, calcium, or their hydrides, as promoters.³ The liquid phase process, employed by Monsanto, Phillips, and Du Pont, uses a paraffinic or cycloparaffinic solvent, or hydrocarbon diluent. The vapor phase process, used by Union Carbide, is claimed to have advantages in capital equipment (25%) and operating costs (15%) over the liquid phase processes.³

The importance of the different HDPE processes and the costs involved lies particularly in the possibility that the HDPE crosslinking would be carried out "in house", i.e., by the HDPE manufacturers themselves. In this case, the difference of a few cents a pound in cost of manufacturing the HDPE is significant, since the manufacturer having the lowest cost HDPE

process could conceivably also produce (and sell) the crosslinked HDPE for less. Most of the crosslinking processes to be considered will be viewed as if they actually would be conducted "in-house", with Monsanto's HDPE manufacturing process used as an example. Details on the Monsanto HDPE process and potential for inclusion of the crosslinking step in it were obtained by a visit to the Monsanto Texas City HDPE plant, and discussions with knowledgeable HDPE personnel there.

3.1.5.3 HDPE Crosslinking Methods and Projected Costs

Each of the three general HDPE crosslinking methods investigated in this program or in Phase 1 (silane-grafting/crosslinking, peroxide crosslinking and radiation crosslinking) will be discussed briefly and the projected cost figures given. Any cost figures given that are identical to those cited in previous reports have been reconfirmed with the appropriate sources, so that they are still valid as of February 1978.

3.1.5.3.1 Silane-Grafting and Crosslinking of HDPE

It has been determined, both as a result of a visit to Monsanto's Texas City HDPE plant and also from the experimental results obtained in this program, that the silane-grafting/crosslinking procedure could be integrated into a normal HDPE production line, without any appreciable added capital equipment costs. The only additional costs would be those of the materials used, and probably a small cost for the additional handling, etc. involved.

Before giving these estimates, some discussion of the usual Monsanto HDPE processing is required. At Monsanto's Texas City plant, there are three HDPE polymerization reactors and processing lines which together produce about 180 million pounds per year of HDPE, using the liquid phase process. The polymer produced is filtered and dried to a powder before further processing. This is the same Monsanto HDPE powder which was used for form-stability processing in this project. Of course, it is not ordinarily isolated separately, but instead is carried through the complete process to give the finished HDPE pellets.

On two of the three HDPE lines, this processing involves mixing of the PE powder with required additives (stabilizers, anti-static agents, etc) in large Banbury mixers (capacity ~350-400 lb) for about 2 min in the melt, followed by extrusion and chopping of the HDPE into pellets (in 90°C H₂O). The finished pellets are then dried and blended as needed to meet specifications, prior to shipping.

The silane-grafting/crosslinking procedure would be integrated as follows. The silane (and the other components) would be added to the PE in the Banbury mixers (as was done in the lab on a small scale). This mixture would then be extruded (estimated extruder dwell time ~1-2 min), again as was done on a small scale. The crosslinking reaction would be carried out as the extrudate is chopped into pellets in the 90°C H₂O. Here, the dwell time is short (<1 min) but small scale test results in this project indicate that it should be sufficient to insure adequate form-stability. In addition, a faster-reacting silane (vinyl trimethoxysilane) would be used in place of the vinyl triethoxysilane employed here. The crosslinked PE pellets would then be dried, as at present, to give the finished, form-stable HDPE product.

There are some minor changes or additions that would have to be made to the processing line in order to permit the silane grafting/crosslinking step to be incorporated. One is to add a pre-mixer to the Banbury mixer. The second is the addition of a line going from the extruder to a methanol recycling unit. This is required since the methanol (or ethanol) produced in the crosslinking reaction (by hydrolysis of the grafted vinyl trimethoxy- or ethoxy-silane) could not be "dumped" but would have to be recycled instead. A methanol distillation unit is in operation to recycle methanol from the polymerization reactors, so that only a line to the unit would be needed. The estimated capital costs for these additions (as provided by Texas City personnel) are ~\$100,000. On a per pound basis (over 10 years) these costs are essentially negligible.

An explanation of the other costs listed in the cost estimate, given in Table 7, is as follows. The basic cost-of-goods sold (COGS) is Monsanto's COGS for the liquid phase HDPE process. It includes the cost of standard additives, such as stabilizers and anti-static agents, which add only 0.15¢/lb to the HDPE cost. As mentioned previously, it is believed that these should be included, based on stability test results in this program. Also, very little would be saved by eliminating them. A roughly estimated 1¢/lb additional "burden" for handling storage, etc., the silane (and other materials used in the silane-grafting/crosslinking process) is added to the basic COGS, also.

The silane-grafting materials cost estimate is a "package" estimate provided by Dow Corning for large volume (>1 million pounds/year) production and includes the cost of materials and royalty fees on their patents. Dow Corning is, as far as could be determined, the only U.S. producer of vinyl trimethoxysilane (VTMS, which would be used in any actual large-scale production, rather than VTES). VTMS normally sells at \$5.07/lb in 500-lb drums, so that this "package" price represents the

Table 7. ESTIMATED COSTS AND SELLING PRICES FOR FORM-STABLE HDPE-TES
PREPARED BY VARIOUS IN-PLANT CONVERSION ROUTES

Cost Element	Process		
	Silane-Graft/ Crosslink (¢/lb)	Peroxide Crosslink (¢/lb)	Radiation Crosslink (¢/lb)
1. COGS - Basic HDPE Resin	23.6 ^(a) (19.6) ^(b)	23.6 ^(a) (19.6) ^(b)	23.6 ^(a) (19.6) ^(b)
2. Added Materials Cost	8.0 ^(c)	1.4 ^(d)	0
3. Added Materials Handling Cost	1.0	0.2	0
4. Added Capital Equipment Costs	0 ^(e)	0	0
5. Radiation Crosslinking Cost (includes capital equipment)	0	0	1.0 ^(f)
Total Cost to Manufacture	32.6 ^(a) (28.6) ^(b)	25.2 ^(a) (21.2) ^(b)	24.6 ^(a) (20.6) ^(b)
6. Estimated Selling Expenses and "Profit"	<u>1.4</u>	<u>1.4</u>	<u>1.4</u>
Final Estimated "Selling Price"	34.0 ^(a) (30.0) ^(b)	26.6 ^(a) (22.6) ^(b)	26.0 ^(a) (22.0) ^(b)

(a) Liquid Phase HDPE Process (Monsanto).

(b) Vapor Phase HDPE Process (Union Carbide).

(c) Materials: Vinyltrimethoxy silane, benzoyl peroxide, dibutyl tin dilaurate (+ royalties to Dow Corning).

(d) Lupersol 130 Peroxide.

(e) \$100,000/10 yr/5,000 lb/hr = 0¢/lb.

(f) Volume $\geq$ 10,000,000 lb/yr, 10 Megarad dosage.

lowest cost figure obtainable. This is true even if the VTMS concentration to be used were lower than the VTES concentration (e.g., 1.5-2 phr vs. 3 phr) employed previously. It is expected that the silane concentration could be lowered somewhat since, of course, the VTMS molar concentration is higher than the VTES concentration at the same weight level.

For comparative purposes, a cost estimate is also given for the vapor phase HDPE process (Union Carbide), whose COGS is estimated by Texas City HDPE personnel to be ~4¢/lb less than Monsanto's. To both of these costs to manufacture, a very minimal estimated 1.4¢/lb selling expenses and "profits" are added, bringing the totals to 34¢/lb and 30¢/lb, respectively. This selling price and minimal profit level represents one which might be negotiated for very large-scale purchases (e.g., $\geq 10,000,000$ lb/yr).

It should be pointed out that actual selling prices may vary and will be largely determined by market conditions, as well as by order volume. Current prices for HDPE from major producers are around 28¢/lb (in bulk) but possibilities for negotiating lower prices for very large quantities do exist. Further, even though Union Carbide's vapor phase HDPE may cost less to produce, they will no doubt sell it at prices comparable to the majority the HDPE sold, if they can do so.

3.1.5.3.2 Peroxide Crosslinking of HDPE

For comparative purposes only, a cost estimate is given in Table 7 for peroxide crosslinking of HDPE, even though this process is the least favored among the three being considered. The reasons for this are: (1) the crosslinked products obtained were somewhat inferior to those obtained by the other two processes; and (2) control of the process (presuming it is done via extrusion crosslinking on a regular HDPE processing line) on a large scale could be more difficult than the other two crosslinking methods discussed. Again, the same assumptions were made as discussed previously in the silane-grafting/crosslinking process, and the same "cautions" apply in regard to final "selling" prices estimated to be 26.5¢/lb and 22.5¢/lb respectively, for the liquid and vapor phase HDPE processes.

3.1.5.3.3 Radiation Crosslinking of HDPE

The third processing method and projected costs to be considered are those of radiation crosslinking. As demonstrated in this project, the radiation crosslinked HDPE products are superior to the peroxide crosslinked HDPE products (investigated in Phase 1), and only slightly inferior to the silane-grafted/crosslinked HDPE products in terms of percent ΔH_f retained. Radiation

crosslinking is also a process which would be readily amenable to large-scale production (as well as small-scale) and therefore should be given serious consideration.

The cost estimates given in Table 7 are again based on "in-plant" production of the crosslinked HDPE product; the radiation crosslinking presumably would be carried out, in this case, on the pelletized HDPE, rather than prior to pelletizing as with the other two processes. The capital equipment costs for the appropriate radiation equipment are included in the "Radiation Crosslinking Cost" estimate; this information was furnished by Dr. Kennard Morganstern of Radiation Dynamics, Inc. The 10 megarad dosage was demonstrated in this project to be adequate to insure form-stability (with 0.9 M.I. HDPE).

An alternative to carrying out this crosslinking process "in-plant" by the HDPE producers themselves is to purchase the finished HDPE pellets and irradiate them in a separate operation at another site. While this is certainly feasible and might well be done initially until sufficient product volume was generated to warrant "in-plant" production by the HDPE manufacturers, there are some disadvantages to it. In order to obtain the HDPE pellets at a price below normal market price, either "second" or "off-spec" HDPE would have to be purchased, or large volume contracts with the HDPE manufacturer would have to be negotiated. While "off-spec" HDPE (such as the products tested in this program) is generally available for 22-24¢/lb, it has the drawbacks of uncertainty in quantities available and lack of product uniformity. Thus, its use is not recommended, particularly if large volumes were to be involved.

For very high volume HDPE usage ($\geq 10,000,000$ lb/year), it is possible to negotiate favorable prices (below market levels) with the HDPE manufacturers. It has been indicated by one company (not Monsanto) that HDPE purchase prices of 25-26¢/lb for this type of volume are reasonably realistic. However, this would still result in a higher total cost than the "in-plant" irradiation crosslinking cost, since shipping and handling charges (as well as profit on resale) would have to be added.

Therefore, using the most favorable "in-plant" production costs in all cases, for the three form-stable HDPE processing methods (with the liquid phase, (Monsanto) HDPE process), the resulting estimated final large volume ($\geq 10,000,000$ lb/year) "selling prices" are as follows: (1) radiation crosslinking - 26¢/lb; (2) peroxide crosslinking - 26.5¢/lb; and (3) silane-grafting/crosslinking - 34¢/lb. Thus, it appears that the radiation crosslinking process has a cost advantage of at least 8¢/lb over the silane-grafting/crosslinking process. Although

slightly inferior to the silane-grafting process in terms of ΔH_f retained, it may well be that, if cost is the primary factor of importance, then radiation crosslinking would be the favored method for large-scale production of a crosslinked HDPE TES material.

3.2 TASK 5, EXTENDED THERMAL CYCLING OF THE 250 LB HDPE-TES PELLET BED

Evaluation of the 250-pound lot of silane-grafted and cross-linked HDPE, selected as the prime candidate for energy storage in Phase 1, was carried through more than 600 melt/freeze cycles in the 60-gallon TES unit. The durability and long-term stability of the polymer, and particularly the effect of repeated thermal cycling through the melting point on heat of fusion and crystallinity (and thus the thermal storage capacity), were determined by heating and cooling the unit between 145°C and 105°C. These temperatures were selected to simulate actual use conditions, but the test was conducted at an accelerated rate of about twelve cycles per day.

Differential scanning calorimetry is probably the best analytical method to detect changes in ΔH_f and the thermal storage capacity. The measured ΔH_f of the polymer after 632 cycles, 47 calories per gram, is slightly higher than the 46 cal/gram value found before thermal cycling, as shown in Table 8. This difference is small, and within experimental limits, but it may represent a slight but real increase in crystallinity due to annealing.

Some adhesion of the pellets, as shown in Figure 5(a) was seen after 632 cycles, but this effect was limited to a thin layer at the top of the tank. The great majority of the pellets remained discrete and free-flowing, as shown in Figure 5(b).

Table 8. Differential Scanning Calorimetry ΔH_f Values for Silane-Grafted/Crosslinked HDPE in the 60-Gallon TES Unit

<u>Melt-Freeze Cycles*</u> <u>(No.)</u>	<u>ΔH_f^{**}</u> <u>(cal/g)</u>
0	46
170	44
632	47

*Cycled between 105°C and 145°C.

**See Table 6 for DSC Conditions Used.

- (a) A one inch thick skin of slightly sintered HDPE pellets was formed at the top of the storage chamber only, but not in the rest of the 60-gallon storage tank.

- (b) Except for the thin sintered layer at the top of the chamber, shown in 5(a), the great majority of the HDPE pellets in the 60-gallon storage tank remained unbonded, free-flowing, and discrete after 632 melt-freeze cycles, as shown here.

Figure 5. Views of a small skin of HDPE pellets from the top and the majority of free-flowing HDPE pellets taken from the 60-gallon TES unit tank after 632 melt-freeze cycles.

Pellets in the top region are subjected to the maximum temperatures and pressure due to the heat exchange flow path and the buoyancy of the polyethylene pellets in the slightly higher density ethylene glycol. Similar to those seen in earlier experiments in Phase 1, the agglomerates were weakly bound and easily broken up, and were at worst loosely knit, open structures. The particles retained their original form and shape. The slight adhesion did not interrupt the free flow paths around each particle and would have no adverse effect on the performance of the pellet bed. Melt-freeze cycling in the 60-gallon unit has, in fact, been resumed.

Delays due to mechanical problems limited this test to less than the desired 1000 cycles. Nonetheless, the test data and visual observations of the polymer confirm the earlier small-scale test indications that ΔH_f values, after repeated melt-freeze cycling, are at least as high as those of the original polymer and that there was no observable adverse effect on the HDPE's durability or heat storage capability after 632 melt-freeze cycles.

3.3 TASK 6, AIR THERMAL TRANSFER MELT-FREEZE CYCLING OF THE FORM-STABLE HDPE-PELLET BED

A relatively minor effort was performed to demonstrate and evaluate the use of air thermal transfer for the heating and cooling of a HDPE TES pellet bed. The objective was to demonstrate the feasibility and show the system was adequate with respect to thermal stability, thermal transfer, thermal form stability, and storage capacity. It was expected that such a bed would work, but thermal stability in air, the poor heat transfer of air, and the weight of the bed material in itself needed to be examined. This was in contrast to the more desirable and already defined utility with liquid thermal transfer where the polyethylene pellets are in a bouyant condition.

To illustrate air thermal transfer, a small TES bed of form-stable HDPE pellets was made up and exposed to heating and cooling cycles that included the 130°C melting point of the HDPE. Air at 300°C was pumped into the device for heating and room air at ~20°C for cooling. Cooling curves were determined after the pellet bed was first melted (charged), and the heat of fusion of the pellets was measured after 25 melt-freeze cycles to validate the retention of the storage characteristics.

The experimental bed is shown in Figure 6. The bed consisted of 400 grams of form-stable, but otherwise unstabilized, HDPE TES pellets identified as No. 3-B. The pellets were packed

Figure 6. View of insulated laboratory-scale air thermal transfer system for melt-freeze cycling of a form-stable HDPE pellet bed.

into about a 12 inch length of a 36 inch long by 2 inch diameter vertical Pyrex glass tube, and confined at the ends by an open mesh screen. Air flow for both heating and cooling was in the same direction, downward, through the column. Heating was provided by a laboratory heat gun modified for control of temperature with a constant air flow. The temperature of the air coming out of the gun was in the range of 300°C, and the delivered air flow about 10 cubic feet per minute. The entire column was insulated with 1 inch of fiberglass covered with aluminum.

Temperature was measured only at the outlet, with a thermocouple just below the level of the confined pellets. Establishing that heating (charging) was achieved in each cycle was accomplished by visual observation through windows at points along the column. The observation consisted of determining that the pellets had changed from a white opaque color to transparent; the latter condition indicated that they were melted. Other color changes, implying degradation, could also be noted if evident.

Thermal cycling of the HDPE-TES bed consisted of first heating the column by blowing the heated air through it. This was rather inefficient since high air flow rates could not be achieved through the bed and there was a limit of 200°C to which the pellets could be subjected. Air flow was restricted because of the column back pressure and heating above 200°C would have surely caused degradation of the HDPE (although not necessarily reducing the heat of fusion significantly). Accordingly, as expected, providing accelerated thermal cycling was not possible, as was the case for liquid thermal transfer (earlier accomplished). However, the column was generally heated in 60 to 80 minutes. The end point of the heating state was an observation that all pellets were melted.

The second stage of the thermal cycling was cooling, whereupon measurements were made. The same air pressure as was used in heating was maintained (with some little change in flow rate due to expansion of the beads). Air at 20°C was introduced. A typical cooling curve is shown in Figure 7. This graph shows the points in time when it was observed that the TES pellets were refrozen at the top (1) and the bottom (2) observation ports.

The column of 400 grams of pellets had 16,000 calories available from its heat of fusion and ~10,000 calories from specific heat over the temperature range from 130°C down to 80°C. Thus, it should have been able to increase the temperature of ~4000 grams (3×10^6 cc) of air from 20 to 60°C. That this was achieved (assuming some heat losses) is illustrated in Figure 7, where air was maintained at above 60°C for a period of one hour.

Figure 7. Cooling curve for a bed of melted HDPE-TES pellets using air thermal transfer.

Thermal cycling of the bed through the melt was conducted 25 times in the above manner. At the conclusion of the 25 cycles, the column was disassembled and pellets removed from the lower third for tests. The heat of fusion was measured by DSC and shown to be at least 95% of the initial value, indicating an acceptable retention. The pellets from the top hot zone were also examined and noted to be discolored somewhat on the surface. This was obviously due to overheating (greater than 200°C); the thermal insulation in this region also darkened, indicating that temperatures of at least 250°C were reached. The particular pellets contained none of the thermal stabilizer or antioxidants usually present in HDPE because they were made from the HDPE intermediate. Thus, as expected, for air thermal transfer where oxygen is readily available, the usual product stabilizers must be included.

A relatively high temperature drop across the bed also indicated the high back pressure due to the bed and the insufficient thermal transfer in and out of the particular pellets. Thus, TES beds for air would best be designed using small pellets with a higher surface-to-volume ratio and low length-to-diameter ratio columns to achieve adequate heat exchange rates, and air flows that would take maximum advantage of the melting transition temperature of the HDPE. Utility of the HDPE-TES material, using air thermal transfer, was thus indicated.

3.4 TASK 7, LONG RANGE ALTERNATE SOURCES FOR ETHYLENE (AND POLYETHYLENE)

Ethylene is currently in ample supply, and is expected to be so for the next 10 years (see section 3.1.5). This excess supply situation is not expected to continue indefinitely, however, as the availability of the petroleum and natural gas feedstocks from which ethylene is currently produced decline. Thus, there is concern whether or not alternate sources of ethylene will be available long-range.

The exact time at which a switch to alternate ethylene sources will have to be made cannot be predicted, but will come when alternate routes become competitive economically with the present ones, due to scarcity and high prices of gas and petroleum. Even now, South Africa is deriving 20-25% of its gasoline and petrochemical requirements by Fischer-Tropsch synthesis, using a coal-derived synthesis gas as feed stock.⁴

In order to verify that alternate synthesis routes to ethylene do exist and are indeed technically feasible (even though not at present economically competitive) one of the tasks of this program was to define such routes. Accordingly, a literature

search was performed by computer on alternate sources (other than petroleum and natural gas) for ethylene and/or other hydrocarbons. The data bases searched are listed at the conclusion of the supplementary bibliography. From these ~1000 report titles of potential relevance were generated. On further inspection, nearly half were eliminated as not specifically relevant, and many of the rest were duplications. Those articles and patents which appeared most pertinent were obtained and reviewed. A supplementary bibliography of citations, deemed relevant, is attached, classified according to "source" of ethylene. Duplications and most foreign-language references, except German and French, were not included.

The discussion of alternate ethylene sources will, of necessity, be limited to brief summaries. The discussion is divided into three broad "source" categories: (1) plant and biomass sources; (2) coal sources; and (3) other sources. The first and second categories are the most extensive while the third is very minor. They will be discussed in the order given.

3.4.1 Plant and Biomass Sources for Ethylene

Plant and biomass sources for ethylene may be arbitrarily divided into two general categories: (1) where the ethylene or other hydrocarbon is produced directly by the living plant itself; and (2) where plant or other biomass products are used to produce the ethylene indirectly. The second category fits under the general heading of "biomass conversion" (which also includes waste animal matter), an area of research now being heavily funded by the DOE. The basic technology for ethylene production via "biomass conversion" is well-established. Improvements in costs, yields, etc. are required for it to become economically competitive.

3.4.1.1 Direct Production of Ethylene and Hydrocarbons by Living Plants

Growing plants do produce small, but measureable, quantities of ethylene. Normally, however, the amount produced is too minor to be of significance. For example, in cotton plants, internal ethylene levels of 0.77 $\mu\text{l/l}$ of air have been observed,⁵ and in fungi concentrations of ethylene produced range from 0.18 to 21 ppm.⁶ Thus, the quantities of ethylene obtained, even if increased 10-fold, are not likely ever to be sufficient to consider direct ethylene production by plants as a useful source for industrial purposes.

On the other hand, a number of plants produce hydrocarbon latices of sufficient quantity and quality to be directly useful themselves. The most important is, of course, the

rubber tree, *Hevea brasiliensis*, which produces natural rubber (high molecular weight *cis*-polyisoprene). The yield of this crop has improved 30-fold over the last 15 years, so that Malaysian plantations can now produce 2000 pounds of rubber/acre/year (equivalent to about 10 barrels of oil).⁷ Although it would be possible to break down natural rubber into simpler hydrocarbons (from which ethylene could be synthesized), the value of natural rubber itself would, for the most part, rule out its use in this manner.

Other hydrocarbon producing plants, particularly those producing lower-molecular weight hydrocarbons, might well be considered for this purpose instead. In the genus *Euphorbia* (a member of the same plant family as the rubber tree) nearly every species produces a hydrocarbon latex, and most of these are much lower in molecular weight than natural rubber.⁷ Furthermore, many of these plants can be grown in arid regions of the United States (such as the Southwest) and thus would not compete for food-producing cropland. The hydrocarbons obtained from these plants could be used just as crude oil is now-refined, extracting the sterols which it contains, and "cracking" the rest to ethylene, propylene, etc. It is estimated, since the plants contain 2-10% by weight of hydrocarbon, that one acre producing 50 tons of the plants per year would yield up to 5 tons of hydrocarbon/acre/year, or the equivalent of 2 barrels of oil. With improved cultivation and genetic selection, this could probably be increased to 10 barrels or more.⁷

There are other hydrocarbon producing plants, such as the Gayule plant, which can be grown in the arid regions of the southwestern United States and northwestern New Mexico, and produce higher molecular weight hydrocarbons (*cis*- and *trans*-polyisoprene). These may also be considered as potential alternate ethylene sources. Factors such as ease of cultivation, yield of crops and hydrocarbons, ease of breakdown of the hydrocarbons into lower molecular weight compounds, etc., would determine which, among these various possible hydrocarbon-producing plants, would be most suitable to use for producing ethylene. Of course, cost and yield comparisons with other potential alternate routes to ethylene would have to be made, to decide if this method is at all competitive economically.

3.4.1.2 Indirect Methods for Obtaining Ethylene and Other Hydrocarbons from Plant or Other Biomass Sources

While the direct production of hydrocarbons by plants may appear to be the simplest route to ethylene, other, less direct methods are well developed and may, in fact, be more economical. These methods fall under the general heading of "biomass conversion" (which may also include use of animal wastes). Currently, DOE is extensively funding research in this area, through

The Division of Solar Energy's Fuels from Biomass (FFB) Branch. The July 27, 1977 Program Plans of this Branch listed projected budgets of \$20.7 million for FY 1978 and \$52.1 million for FY 1979, with most of the increase targeted for thermochemical development and fermentation.

To discuss any of these individual DOE research programs, which may result in alternate routes to ethylene, would be an unnecessary duplication of effort; a listing of reports available from NTIS may be found in the supplemental bibliography. It may suffice instead to cite the overall objectives and scope of the FFB program (as given in the above July 27, 1977 report) and mention one or two examples pertinent to ethylene synthesis.

"The overall objective of the FFB program is to develop the capability for converting biomass resources into clean fuels, petrochemical substitutes, and other energy-intensive products that can supplement similar products made from conventional fossil fuels. The scope of the R&D efforts has included three main areas:

- . Growing terrestrial and aquatic crops in energy farms.
- . Harvesting, collecting, transporting, and storing biomass.
- . Converting biomass to fuels and petrochemical substitutes.

The FFB program currently includes only the R&D stages of obtaining biomass and producing fuels from it. Other groups within ERDA (DOE) and other agencies have been responsible for federal activities related to the development and use of incentives to assist technologies in the commercialization stage.

The overall goal of the FFB program is to develop and demonstrate technologies that will lead to the production of 10 quads from biomass, or 5.6 percent of projected energy demand by the year 2020.

Initially, the program will investigate the technical and economic feasibility of collecting and harvesting significant quantities of biomass by a direct combustion demonstration program. The product priorities, however, are liquid transportation fuels (LTF), synthetic natural gas (SNG), and other energy-intensive fuel products and chemicals.

The following supporting goals have been established:

- . To produce an assured supply of biomass on energy farms at a price not to exceed \$1 per million Btu by the year 2000.
- . To produce, with terrestrial biomass as feedstock, liquid transportation fuels (alcohol) at a total cost not to exceed \$3.50 per million Btu (1977 dollars) by the year 2000.
- . To produce, with terrestrial biomass as feedstock, SNG at a total cost (through conversion) not to exceed \$3 per million Btu (1977 dollars) by the year 2000.
- . To produce energy-intensive fuel products and chemicals on a cost-competitive basis by the year 2000.
- . To produce, with terrestrial biomass as feedstock, electricity through direct burning at a total cost (through conversion) not to exceed \$3.50 per million Btu (1977 dollars) by the year 1990."

One important area of FFB research, sponsored by DOE, that is relevant to ethylene production, is that of fermentation of biomass. The goal is to reduce the cost of producing ethanol by fermentation by providing a cheaper source of the sugar used. This source is cellulose, which can be hydrolyzed to glucose, a desirable sugar for fermentation. This hydrolysis is best done enzymatically, and since the cost of enzymes is high, searching for better organisms is important (Program Summary, FFB Branch, Division of Solar Energy, September 1977). The ethanol so produced by fermentation is readily converted to ethylene.

It is now certainly possible to convert the sugar from sugar cane into ethanol, with considerable mass loss but little loss of energy, as shown in the following reactions.⁸ The ethanol is then readily converted to ethylene by dehydration.

Ethylene can readily be produced from alcohol (and vice versa) but from about 1955 up to the present, industrial alcohol has been produced from ethylene, rather than sugar cane, simply because that process was cheaper. As the price of ethylene from petroleum is increased, however, producing the alcohol by fermentation and then ethylene from it may well become competitive economically. It is already estimated that in Brazil the production of alcohol from sugar cane will reach 1 billion gallons by 1980.⁸

Thus, the technology for ethylene production from a plentiful, renewable, natural source (i.e. sugar cane) exists. It may itself be improved upon to make it more economical, and/or may be supplemented by use of the other sources of ethanol (and thereby ethylene) previously mentioned (cellulosic wastes, etc). Additional references to ethanol/ethylene production from plants sources and animal wastes are given in the supplemental bibliography.

3.4.2 Ethylene from Coal

While coal is not a "renewable" resource as are living plants, estimates are that worldwide coal reserves far exceed those of petroleum and natural gas, and will last many more years. Importantly, United States reserves are considerable, enough for >200 years. With the recent emphasis on "energy independence" coal is therefore being considered again as an important energy and chemical raw material source, both directly as a fuel, and indirectly by gasification and liquefaction processes. Although some of the technology is actually quite old, considerable research is now being done (much of it funded by DOE) to improve the efficiency and economics of these existing processes. These processes will be described under the general categories of (1) coal gasification processes and (2) coal liquefaction processes.

3.4.2.1 Coal Gasification as an Alternate Ethylene Source

Prior to the widespread availability of petroleum hydrocarbons as raw materials, a common route to ethylene (and many other chemicals) was via acetylene from coke (obtained by burning of coal):

This process was used extensively by Germany in World War II. However, it is not as favored now, in comparison with other coal gasification and liquefaction processes.

One of the principal routes to ethylene from coal gas is the Fischer-Tropsch process (also utilized by Germany in World War II), an outline of which is given in Figure 8.⁹

Figure 8. Fischer-Tropsch process for ethylene synthesis from coal (Catal. Rev.-Sci. Eng., 14, 153 (1976)).

This process generates carbon monoxide and hydrogen (synthesis gas) by treating coal (or coke) at high pressure with steam. The CO/H₂ stream is purified to remove CO₂ and sulfur-containing poisons, and the desired H₂/CO rates are obtained via the "water gas shift" reaction. With appropriate choice of catalyst and reaction conditions the product distribution can be altered to maximize production of the desired chemical compound (e.g., ethylene). Some of the more important synthesis reactions (and also some concurrent complicating reactions) which can occur with this process are as follows:⁹

REACTIONS IN FISCHER-TROPSCH PROCESS

1. Synthesis Reactions Which Can Occur

Methanation:	$3\text{H}_2 + \text{CO} \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$
Paraffins:	$(2n+1)\text{H}_2 + n\text{CO} \longrightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$
Olefins:	$2n\text{H}_2 + n\text{CO} \longrightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$
Methanol:	$2\text{H}_2 + \text{CO} \longrightarrow \text{CH}_3\text{OH}$
Higher alcohols:	$2n\text{H}_2 + n\text{CO} \longrightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}$

2. Complicating Reactions in CO Hydrogenation

Water gas shift:	$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$
Boudouard reaction:	$2\text{CO} \longrightarrow \text{C} + \text{CO}_2$
Coke deposition:	$\text{H}_2 + \text{CO} \longrightarrow \text{C} + \text{H}_2\text{O}$
Carbide formation:	$x\text{M} + \text{C} \longrightarrow \text{M}_x\text{C}$

The exact mechanism of the Fischer-Tropsch synthesis is still debated, even after 50 years. One model assumes that CO and H₂ interact on a metal (M) surface to produce a CH₂O species (in

the enol form) and that chain growth occurs by surface condensation reaction with other CH₂O complexes.⁹

There is a considerable amount of research being done now on improving this process and the economics of it, via more effective catalysts, etc. Additional references to some of the work in this area may be found in the bibliography.

At present, there is one commercial Fischer-Tropsch plant, the SASOL in South Africa, where the combination of large coal reserves, no petroleum resources, etc., has made it economical to develop a fuels and chemicals economy based on coal gasification, followed by Fischer-Tropsch synthesis. Thus, it would appear that this is one of the alternate routes to ethylene that will very likely be utilized in the future, as petroleum resources dwindle.

In addition to the Fischer-Tropsch process, other processes may be used to obtain ethylene via coal gasification. Included among these is methanol homologation to ethanol, followed by dehydration.¹⁰ A schematic diagram of this process is shown in Figure 9.

Figure 9. Ethylene production from coal via methanol homologation (Chemtech, May 1, 1977, p. 295).

A coal-based methanol plant (which is available using current technology) provides methanol to be carbonylated to ethanol and higher alcohols (again, based on current technology; e.g., Monsanto produces acetic acid via methanol carbonylation.)¹⁰ The ethanol is then dehydrated to ethylene, as in ethylene production from sugar cane. While this process is not now employed commercially, estimates have been made that a typical plant based on it could produce 1 billion pounds/year of ethylene plus lesser amounts of propylene, butanol, and acetic acid.¹⁰

Other gasification processes which have been studied and which offer potential alternate routes to ethylene include: (1) low-temperature ($<200^{\circ}\text{C}$) gas evolution from coal, producing primarily methane, but also, higher hydrocarbons¹¹; (2) a multiple-catalyst system for converting coal to methane in the presence of steam¹²; and (3) a non-catalytic hydrolysis of coal to produce methane and benzene.¹³ These are not the only potential processes. Others are included in coal gasification and liquefaction review articles listed in the main bibliography.^{14,15}

3.4.2.2 Coal Liquefaction Processes

In addition to the coal gasification routes to ethylene discussed above, it would also be possible to obtain ethylene by "cracking" liquid hydrocarbons produced directly from coal, much as is now done with petroleum hydrocarbons. Gasification and liquefaction of coal are, of course, not mutually exclusive processes; both may occur together, with some of the products being used directly as fuels and others as chemical feedstocks, as illustrated by Figure 10.¹⁴

The primary coal liquefaction processes, which may provide additional routes to ethylene, will be described briefly. Again, basically, this is not a new concept or process; Germany used direct coal hydrogenation for the production of oils (liquid fuel) during World War II.

Some of the processes by which liquids are produced from coal are: (1) pyrolysis at successively higher temperatures ($315\text{--}840^{\circ}\text{C}$) in fluidized-bed reactions,¹⁵ (which may be combined with hydrogenation); (2) dissolution in a heavy aromatic solvent under moderate hydrogen or synthesis gas pressure;¹⁵ (3) catalytic coal liquefaction using synthesis gas¹⁶ (in which high-sulfur bituminous coal is liquified and desulfurized by hydrotreating with synthesis gas at $400\text{--}450^{\circ}\text{C}/3000\text{--}4000$ psi in the presence of cobalt molybdate and sodium carbonate catalysts, steam, and a recycle oil); and possibly (4) supercritical gas phase extraction (based on the enhancement of volatility by compressed gases), which is proposed for extraction of coal to produce chemical feedstocks and liquid fuels, and for extraction of oil from shale.¹⁷

As stated previously, these liquid hydrocarbons as produced by whatever method from coal, would still have to be "cracked", as is now done with petroleum hydrocarbons, to give the desired end-product, ethylene. Whether it would be preferable to produce ethylene in this manner, or as described previously via coal gasification routes, would depend on a number of factors: the relative economics of each, which products would be more desirable (or in greater demand) for use as a fuel, etc. It

Figure 10. Schematic diagram of routes to "clean fuel" from coal (Oil and Gas Journal, Aug. 26, 1974, p. 73).

is likely that the type of coal available (e.g. high versus low sulfur, etc.) would be an important factor and the most advantageous and economical routes to ethylene would depend on the situation. Additional coal gasification and liquefaction process references are given in the supplementary bibliography.

The commercial potential of a coal liquefaction process may be demonstrated yet this year with a pilot plant scheduled for 1978 start-up in Catlettsburg, Ky., which will convert 600 tons of high sulfur coal to 2200 barrels of low-sulfur synthetic crude oil daily (to be funded in part by DOE). Hydrocarbon Research, the developer, estimates that a commercial plant producing 100,000 barrels/day of synthetic crude oil could be ready by 1983 (Research/Development, December 1977, p. 6).

3.4.3 Miscellaneous Additional Routes to Ethylene

In addition to the chief alternate ethylene sources already described (plants or biomass and coal), there are a few additional, but relatively minor potential alternative sources of ethylene. These are not expected to be as important as the others already considered. Hence, only a brief description of each will be given. These are not necessarily the only other possible alternatives, but represent those where a potentially abundant raw materials supply exists.

One alternate ethylene source not considered under "biomass" is that of cellulosic wastes from urban refuse. It is claimed that treatment of such refuse with carbon monoxide and steam at 250-400°C under 1500-5000 psi pressures yields over 2 bbl of oil/ton (dry, ash-free); this yield of oil is equivalent to 40 weight percent of the available organic matter and is said to be predominantly paraffinic or cyclo-paraffinic.⁴ This oil could, if desired, be "cracked" to obtain ethylene, among other products. In another, similar process, it is claimed that a ton of municipal refuse is converted into more than a barrel of pyrolytic oil, with recovery of inorganics, for a total 90% conversion or reuse of the raw materials.¹⁸

In yet another example of generation and reuse of hydrocarbons from urban rubbish, the methane gas generated from a landfill in Palos Verdes, California, is currently being extracted and purified by Reserve Oil and Gas Company to provide gas for ~2000 homes in the area (Solar Energy Digest, November, 1977, p. 7).

Still another suggested method for utilization of urban waste which may be mentioned involves the recycling of plastic wastes. In this case it is not ethylene which would be obtained, but the final product, polyethylene itself, in a blend

with polyvinyl chloride, polystyrene, and carbon black (approximately equal parts by weight).¹⁹ What is of potential significance is that the ΔH_f (by DSC) of the PE in the blend remains unaffected by the other polymers present, although, of course, there would be a weight and volume penalty with the other materials added. Further, it is claimed that this blend does not degrade easily, even though PVC normally degrades at $\sim 170^\circ\text{C}$. Whether this could be a potentially useful TES material would depend on other factors also: cost, durability, increased volume requirements, etc. Also, it is possible that, at some future time, plastics could be too valuable to be discarded at all; instead, they might be recycled directly.

Finally, another potential source of hydrocarbons, carbonate rock, may be considered in this survey of alternate ethylene sources. It is claimed that CH_4 and heavier hydrocarbons are synthesized by reduction of CO_2 formed by the thermal decomposition of carbonate rock, using waste heat from nuclear reactors and electricity (for H_2O electrolysis) from reactors during periods of minimum consumption.²⁰ This might not be considered as a "high-volume" potential ethylene source if tied directly to nuclear reactors; however, it is somewhat novel in nature and uses plentiful raw materials.

In conclusion, then, it has been shown that a number of alternate routes to ethylene do exist, and for many the technology is well-developed, waiting only for economic justification for their usage. Furthermore, living plants, which are a renewable resource, provide the basic raw materials source for certain of these alternate ethylene routes.

3.5 TASK 8, AN ECONOMIC BENEFIT ANALYSIS OF THE HDPE-TES SYSTEM

The final task in this project was to do a cost/benefit analysis on the HDPE system and, insofar as possible, compare it with other storage systems. This analysis was to be based on readily available literature data for the other systems, and data generated here for the HDPE TES system.

First, the projected costs for a HDPE-TES system, as it now anticipated that it would be used, will be given. Then, comparisons will be made with other storage systems, using air or liquid transfer, as appropriate.

3.5.1 Cost of Proposed HDPE-TES System

As a basis for the cost of the HDPE-TES material itself, the assumption is made that the form-stable HDPE is manufactured by "in-line" radiation crosslinking and is "purchased" for the estimated selling price of 26¢/lb (see section 3.1.5 for details of this cost estimate).

A summary of costs for the proposed liquid transfer HDPE-TES system is given in Table 9, followed by diagrams (Figures 11 and 12) and a brief explanation of the system.

Table 9: COST ESTIMATE FOR HDPE PELLETIZED BED LIQUID THERMAL TRANSFER SYSTEM

<u>Subsystem</u>	<u>Cost, \$</u>
Storage Medium	1000.00
TES Container	350.00
Insulation	250.00
Heat Transfer (pump)	120.00
Heat Transfer Fluid (in pipes)	100.00
Piping	80.00
Controls	<u>500.00</u>
Total	\$2400.00

The above costs do include labor costs for assembly (~\$600.). It is quite possible that such labor costs could be significantly reduced, if assembly of the entire system (rather than the individual components, is considered, and if manufacturing methods are optimized.

Figure 11 shows the entire prospective thermal energy storage subsystem, while Figure 12 is a view of the energy storage tank, containing the HDPE pellets, and associated components. Both are for a liquid thermal transfer system.

It should be noted that while the HDPE-TES system can store and yield thermal energy at temperatures up to 150°C (300°F), its greatest efficiency is in the 120-140°C temperature range, since its melt-freeze temperature is 130° ± 5°C. Thus, its greatest value is for use in absorption air conditioning, where the efficiency of the air conditioning cycle is highly temperature dependent, in the region of 100 to 140°C.

Heating of the storage system can be accomplished using any source that readily provides temperatures up to 150°C, such as concentrating solar collectors, waste process heat, etc. The system can also be used for electric load leveling, by the introduction of an input of immersion heaters (which simplifies the system by elimination of all but two solenoid valves) with an output of hot ethylene glycol.

Table 10 gives additional specifications and a further breakdown on costs for the liquid thermal transfer system materials used - the HDPE and ethylene glycol, the transfer fluid.

Figure 11. View of entire HDPE-TES liquid transfer system.

Figure 12. View of storage bed for HDPE-TES liquid transfer system.

Table 10. PHYSICAL PROPERTIES AND MATERIALS COSTS FOR LIQUID
THERMAL TRANSFER HDPE-TES SYSTEM

1. SYSTEM OUTPUT:

A. Cooling Mode - 250,000 BTU @ >100°C

B. Heating Mode - 400,000 BTU @ > 38°C

(This requirement is 80% of the cooling mode)

2. COST OF MATERIALS:

	Medium	<u>Cost</u> Weight	<u>Quantity</u> Unit	<u>Initial Cost</u> BTU	Total Cost
1	XL-HDPE Pellets	0.26 \$/lb	~240 gal		
2	Ethylene Glycol	<u>0.25 \$/lb</u>	<u>~200 gal</u>		
	Total	2.31 \$/gal	440 gal (3800 lb)	4×10^{-3} \$BTU	\$1,000.00

3. PROPERTIES OF 2 COMPONENT SYSTEM:

Phase Change Temperature: 130°C
 Useful Temperature Range: 120-140°C
 Heat of Fusion : 50 cal/g
 Bulk Density : ~60 lb/ft³ @23°C

Table 11 gives similar materials cost information for an air thermal transfer system. Not only are the materials cost ~\$400 less for air thermal transfer, but the need for an expansion tank is also eliminated, further reducing costs for the system.

Table 12 gives a further breakdown of the other costs in this TES system (for liquid thermal transfer). The costs are based on estimates from the manufacturers of the various components. It is assumed that the tank, plumbing, and other components are prefabricated and insulated in a factory, with only plumbing (4 lines) and electrical connections (120V) to be made on site.

With the above cost breakdown on the HDPE TES system it is now possible to make a cost comparison with other liquid or air thermal transfer storage systems. Where more exact literature data (and, from a limited search, actual storage systems cost data is not readily obtainable) is not available, estimates of systems costs will be derived from costs for the same or similar equipment, given for the HDPE-TES system, combined with the appropriate materials costs.

3.3.2 Cost Comparisons for Liquid Thermal Transfer Storage Systems

The liquid thermal transfer storage system outputs will all be kept constant at 250,000 BTU, and projected for the 120-140°C temperature range, at which the HDPE TES system is optimally operative. To be considered are: ethylene glycol (EG) alone, rocks, an inorganic salt hydrate (both with ethylene glycol liquid heat transfer) and water alone. Table 13 gives the projected cost estimates for these systems.

The cost estimates are derived from literature data (as indicated in the tables) and from our own calculations, based on the costs for the HDPE liquid thermal transfer system described here. Some explanation of the cost of each will be given. The HDPE/EG costs are, of course, essentially the same as cited previously.

The cost of the storage medium for the "rocks" system (70% "rocks", 30% EG by volume) is derived from a literature value for cost of the rocks and the same EG costs as used in the HDPE/EG system. It is the large volume of rocks/EG required to give the same BTU output as the HDPE/EG system that is responsible for the somewhat surprisingly higher storage medium cost. Also, the larger storage tank required contributes to a higher cost of the system overall, compared to the HDPE/EG system. For all of these liquid transfer systems, the cost of controls, insulation, pumps, etc, are considered as being essentially the same, even though there may be slight differences involved,

Table 11. MATERIALS COSTS AND PHYSICAL PROPERTIES OF AIR THERMAL TRANSFER HDPE-TES SYSTEM

1. OUTPUT:

Cooling Mode 250,000 BTU @>100°C

2. COST OF MATERIALS:

	Medium	<u>Cost</u> Weight	<u>Quantity</u> Unit	<u>Initial Cost</u> BTU	Total Cost
1	XL-HDPE pellets	0.26 \$/lb 1.21 \$/gal	480 gallons 2235 pounds	2.3×10^{-3} \$/BTU	~\$600.00
2	Air	_____	_____	_____	

3. PROPERTIES:

Bulk density: ~40 lb/ft³

Other HDPE Physical Properties: Same as for Liquid Transfer System

Table 12. DETAILS OF ESTIMATED COSTS OF OTHER THAN THE STORAGE MEDIUM FOR
HDPB-TES SYSTEM COMPONENTS FOR 250,000 BTU OUTPUT

<u>Item</u>	<u>Component Parts</u>	<u>Dimensions or Numbers</u>	<u>Cost</u>	<u>Total Cost</u>
TES Container	1. Steel tank	450 gallon - 30 psi	\$285.00	
	2. Internal steel baffles	7 concentric flow diverters	15.00	
	3. Plumbing and control modifications	connectors, fill port, control inserts	50.00	
	4. Expansion tank (opt.)	~45 gallon steel tank	-	\$350.00
Insulation	1. Tank insulation (to 160°C)	tank surface	\$200.00	
	2. Piping insulation (to 160°C)	~30 ft	50.00	\$250.00
Heat Transfer System	1. Centrifugal pump (steel)	10 gpm capacity, 1/3 H.P. -max 5 psi pressure drop	\$115.00	
	2. Filter	-	5.00	\$120.00
Heat Exchanger	none required	-	-	0.-
Heat Transfer Fluid	in pipes only	25 gallon	\$100.00	\$100.00
Piping	1. Steel pipes - 3/4-1 in.	21 ft	\$13.00	
	2. Pipe fittings		30.00	
	3. Installation		37.00	\$80.00
Controls	1. Solenoid valves - 6	120V, 3 way	@\$55.00	
	2. Pressure switches and sensors		@ 35.00	
	3. Relays		@ 20.00	
	4. Thermal Probes		@ 35.00	
	5. Circuit Breaker		@ 25.00	\$500.00
Electric Heaters	none required (unless used for electric load leveling)			0.-
			Total	\$1400.00

Table 13. COMPARISON OF FORM-STABLE HDPE-TES SYSTEM COSTS WITH
OTHER LIQUID THERMAL TRANSFER SYSTEMS

	Storage Medium				
	Output at 130°C				Output at 29°C
	HDPE/EG	Rocks [®] /EG	Ethylene Glycol (EG)	Water [®]	Salt Hydrate ^(x) (CaCl ₂ ·6 H ₂ O)
<u>Characteristics:</u>					
Output, BTU	250,000	250,000	250,000	250,000	~300,000
Vol., gallons	440	1283	1103	788	~300
Weight, lb	3800	24,625	8750	6575	3945 ^(x)
<u>Costs (\$):</u>					
1. Storage Medium					
a. \$/gal	2.31	0.83	2.42	0.02/gal [®] (deionized)	0.05/lb ^(x)
b. Total \$/system	1000.	1060.	2670.	16.00	~200.
2. Storage Tank	350.	980. [®]	880.	1500. ^(a)	350./514. ^(x)
3. Heat Exchanger	none	none	none	90. [®]	450./614. ^(x)
4. Controls, insulation, piping, pump, etc.	~1000.	~1000.	~1000.	~1000.	800./1070. ^(x)
5. Total System Costs	2350.	3040.	4550.	2600. (alternate 1975.)*	1800./2400.
6. Cost, ¢/BTU	0.94	1.22	1.82	1.04 (alternate 0.80)*	~0.60/0.80 1975/1980 Cost Est. ^(x)

References for above estimates:

[®] K. W. Kauffman, "Some Choices of Materials for Thermal Energy Storage, , Solar Engineering, December 1976, p. 19.

^(x) G. A. Lane et al., "Solar Energy Subsystems Employing Isothermal Heat Sink Materials," Final Report, NSF-C906, March 1976,

*G. C. Szego, "Hot Water Systems Group Report," Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings, Charlottesville, Va., April 16-18, 1975. (Note: not for pressurized H₂O).

^(a) Cost estimate for a 9 ft x 4 ft (diameter) carbon steel tank rated to hold 130°C H₂O.

All numbers not referenced above our calculations, based as follows:

Temperature Range: 120-140°C
 ΔT : 20°C
 HDPE : Best reasonable projection-50 cal/g and 26¢/lb, 80% hot volume
 Ethylene glycol : 25¢/lb, $C_p = 0.71$ @135°C
 Rocks : $C_p = 0.21$, $\delta = 2.67$ g/ml, 70% volume, \$15/ton cost[®]
 Volume and Weight: Includes media and heat transfer fluid.

Cost of Ethylene Glycol in piping omitted in all cases.

depending on tank sizes used. The cost of the ethylene glycol in the piping is ignored in all cases.

The EG (alone) system is, as expected, almost twice as expensive as the HDPE system. This comparison shows again the importance of the ΔH_f contribution of the HDPE in efficient energy storage.

The next system to be considered is water alone (except that an ethylene glycol solution is circulated in a closed loop between collectors and storage heat exchanger to diminish corrosion in the collectors). The total system costs for a water system to achieve a temperature of 130°C are slightly higher than that of the HDPE/EG system. An alternate estimate for the cost of a non-pressurized water system is also given, derived from the indicated literature reference. The need for pressurization increases the cost of the storage tank considerably (the estimate of \$1500 was supplied by a local tank distributor). Thus, even water alone in this 120-140°C temperature range is slightly higher in cost as a storage medium than the HDPE/EG system and is about double it in volume.

The data for the $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ system (with EG circulating thru the heat exchanger to the solar collectors), taken from the literature, are presented as what could possibly be expected with a salt hydrate having, as does $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, a ΔH_f of ~ 75 BTU/lb and available at a cost of \$0.05/lb. The "output" and "cost in ¢/BTU" data are really not applicable in the temperature range under consideration (120-140°C), since $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ actually melts at $\sim 29^\circ\text{C}$. This is given simply for comparison in case such a salt hydrate with those properties and melting in the 120-140°C range actually should exist (none was found in a brief literature search). Even in the event such a material were found, the tank holding it would then have to be able to be pressurized beyond the 30 psi rating, cited here for the HDPE/EG system, which would also add to the system costs. Even as shown, the "1980 cost estimate" for this "salt-hydrate" is nearly equivalent to the cost estimate for the HDPE/EG system.

3.5.3 Cost Comparision of Air Thermal Transfer Systems

Table 14 compares costs for three air thermal transfer systems: HDPE, rocks, and a salt-hydrate ($\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, as an example). Here again, the costs cited are derived from literature references, as indicated in the table, or are based on the costs given previously in section 3.5.1 for the HDPE/TES system.

The cost comparison analysis shows that the HDPE system is slightly cheaper than the rock system, and probably about the same as a salt-hydrate system (if one were to exist). The

Table 14. COMPARISON FOR FORM-STABLE HDPE-TES SYSTEMS COSTS
WITH OTHER AIR THERMAL TRANSFER STORAGE SYSTEMS

<u>Characteristics:</u>	<u>Storage Medium</u>		
	<u>Output at 130°C</u>		<u>Output at 29°C</u>
	<u>HDPE</u>	<u>Rocks</u>	<u>Salt Hydrate^(x)</u> <u>(CaCl₂·6 H₂O)</u>
Output, BTU	250,000	250,000	~300,000
Vol., gallons	480	2005	~300
Weight, lb	2235	33,000	3945 ^(x)
<u>Costs (\$):</u>			
1. Storage Medium			
a. \$/gal	1.21	15./ton [⊕]	0.05/lb ^(x)
b. Total \$/system	580.	250.	~200.
2. Storage Tank	~400.	980. [⊕]	350./514. ^(x)
3. Heat Exchanger	none	none	450./614. ^(x)
4. Controls, insulation piping, blower, etc.	~1,000.	~1,000.	800./1070. ^(x)
5. Total System Costs	1,980.	2,230.	1800./2400.
6. Cost, ¢/BTU	0.79	0.89	~0.6/0.8
			1975/1980 Cost Est. ^(x)

References for above estimates:

- [⊕] K. W. Kauffman, "Some Choices of Materials for Thermal Energy Storage," Solar Engineering, December 1976, p. 19.
- ^(x) G. A. Lane et al., "Solar Energy Subsystems Employing Isothermal Heat Sink Materials," Final Report, NSF-C906, March 1976.

All numbers not referenced above our calculations, based as follows:

Temperature Range: 120-140°C
 ΔT : 20°C
 HDPE : Best reasonable projection - 50 cal/g and 26¢/lb, 80% hot volume
 Rocks : $C_p = 0.21$, $\delta = 2.67$ g/ml, 70% volume, \$15/ton cost

primary reason that the "rock" system is more expensive is the 4:1 volume and ~15:1 weight difference involved. The cost of the rocks thus becomes significant, and, of course, the storage tank cost is much higher. Again, the "salt hydrate" used here as an example does not actually melt in the required range but is included for comparison. The total system costs for it, and the cost in ¢/BTU, do not differ very significantly from those for the HDPE system, particularly in the 1980 projected cost estimate. Also, again, system pressure requirements would be higher than for the HDPE, probably adding somewhat to the cost.

Overall then, the HDPE-TES system has been shown to compare favorably to other major potential storage systems: rocks, ethylene glycol alone, water, and a hypothetical "salt-hydrate" system in liquid, or air, thermal transfer in its 120-140°C optimum operating range. It is slightly lower in cost than the "rock" system, about half the cost of the ethylene glycol system alone, lower than the water only system, and competitive with a salt-hydrate system.

While these results may at first appear somewhat surprising, two important factors help to explain it. First, the temperature range (120-140°C) considered was limited to the one in which the HDPE system operates at maximum efficiency. This is also the range suited for solar absorption air conditioning applications, and hence the use of the HDPE TES system for this purpose is recommended. Second, the cost of the storage material itself becomes relatively less important as the size requirements for a storage tank increase greatly (as is the case with "rocks") or with the need for expensive heat exchangers (as with the salt-hydrates). In one study on the economic feasibility of phase change materials (PCM) for thermal energy storage, the authors stated that, "designing a PCM storage system which is economically competitive with water storage will depend primarily on finding an inexpensive way of increasing the effective conductance of the PCM, or of providing multiple conduction paths".²¹ The HDPE TES system does accomplish this goal.

3.5.4 Additional Economic and Conservation Benefits of the Form-Stable HDPE-TES System

Some additional economic and conservation benefits of the form-stable HDPE-TES system may also be cited, which are not directly related to the cost of the system itself. These pertain largely to the increasing need for fuel conservation, as our petroleum and natural gas resources diminish.

If we assume that 1 million HDPE TES storage units might be installed in homes in the USA, each of which has a capacity of one third million BTU, then 330 billion BTU can be stored per use cycle. This is equivalent to 56,000 barrels of crude oil per use cycle. Assuming only a very conservative 150 days per year use (approximately 40%) and also a conservative 20-year life, this HDPE-TES material could save 168 million barrels of crude oil (or the equivalent in other energy forms) over its functional life. This is a savings of 18 pounds of crude per pound of HDPE-TES material.

A more optimistic usage projection and material life (300 days and 30 years) would make this ratio almost 60, for a savings of 560 million barrels of crude oil (or equivalent). These savings are significant, and would increase as more units were installed each year.

Furthermore, these savings are consistent with the conservation of our petroleum resources, especially over the near term. Importantly, the form-stable HDPE TES material could be made available almost immediately (1978) and in conjunction with solar thermal units could initiate savings of our petroleum resources. While it would be unrealistic to assume that the HDPE-TES material is the only or the ultimate answer to thermal energy storage in the long term, it is projected that savings that could be introduced over the next 20-40 years would more than justify its immediate introduction into the market place.

In addition to use in homes for solar heating and cooling, storage devices incorporating the HDPE-TES material could also be used immediately for load leveling from a public utility, thus reducing capital requirements that in themselves require energy. The savings here would not be directly in saving fuel (except that probably more efficient conversion equipment would be used), but in the energy saved in reducing the requirement for additional capital facilities.

Finally, some of the significant advantages of the HDPE-TES system in the applications where it may find the greatest utility may be cited. First, its primary utility is expected to be for solar absorption air conditioning applications, where it has these advantages: (1) the 130°C melting point of the HDPE is consistent with the operating absorption air conditioning at high efficiency; (2) the input from solar collectors for charging need to be no higher than 140°C; (3) the storage system consists only of a simple baffled tank filled with $\frac{1}{8}$ to $\frac{1}{4}$ inch pellets; (4) with ethylene glycol as heat transfer fluid, the system can operate at near normal, atmospheric pressures.

For other potential applications, such as heating and load leveling from a public utility, the following advantages are particularly significant. First, no heat exchangers are required since heat is transferred directly into and out of the pellets, which are in contact with the transfer fluid. Second, for a storage output of one million BTU (liquid heat transfer) only an 1800-gallon storage unit is required, compared to 5100 gallons for rocks, 4400 gallons for ethylene glycol, and 3100 gallons for pressurized water (over the 120-140°C optimum operating temperature range). Third, in addition to pellets, the storage material can be fabricated into a variety of forms, such as baffles, tank liners, etc. to provide additional storage capacity within the system.

Other, general advantages to the use of form-stable HDPE as a TES material may also be cited. It is a relatively low cost (less than 30¢/lb in large volume), readily available polymer, whose basic starting material, ethylene, may be derived from either petroleum, coal, or renewable plant sources. The technology required to introduce form-stability is well-known and can be accomplished on a continuous, large-volume basis.

Thus, the large energy savings potential in home heating and cooling or load leveling uses, combined with the advantages and the favorable economics of the form-stable HDPE-TES system as demonstrated here, should all act as stimuli for its further development and implementation.

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