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THE SEPARATION OF N-PARAFFINS  
FROM PETROLEUM FRACTIONS  
FOR USE AS SUBSTRATE IN PROTEIN PRODUCTION<sup>1/</sup>

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## INTRODUCTION

The production of single cell protein is a subject of widespread current interest. The efforts of many groups have greatly intensified in recent years in preparation for an anticipated large and possibly critical demand for these products.

Many production routes to such materials appear technically viable and are the object of comprehensive examination. The production of single cell protein grown on high purity normal-paraffin substrates using yeast as the microorganism is highly favored by many.

The production of the high purity n-paraffins for use as substrate is a critical step in the over-all production route to the final protein product. The reliability and economics of production and the quality of n-paraffin products are highly influential on the total processing scheme. The separation of n-paraffins from petroleum fractions by means of molecular sieve adsorption techniques has been proven to be an acceptable means for obtaining such n-paraffins.

This paper examines the commercial status of n-paraffin production by means of molecular sieve adsorption, presents a process description of such a process in commercial use and puts forth several significant recommendations for the application of this technology in the protein field.

## I. COMMERCIAL EXPERIENCE

Because the production of single cell protein using n-paraffin as a substrate is highly sensitive to both the cost and the quality of the n-paraffins used, the selection of methods to obtain n-paraffins deserves a great deal of attention in examining the over-all production route from petroleum to protein. The method chosen at the outset should be economic, capable of providing a high quality product, possess a high degree of processing flexibility, and must be proven to be technically and operationally reliable through a solid history of acceptable commercial application across a wide range of sizes of production units.

Hydrocarbon processing plants have from their inception depended upon distillation and scrubbing for the separation of process feedstocks, and the subsequent recovery of intermediate and finished products. Thus, refining processes were initially developed around hydrocarbon fractions of a specific boiling range. The recovery of products having other desirable physical or chemical properties depended upon feedstock selections, and thermal or catalytic conversions.

In more recent times, however, it became possible to separate hydrocarbon streams into specific chemical classes by means of liquid extraction processes. Aromatics extraction plants are an outstanding example of this technique, as well as an example of how refinery operations were modified to take full advantage of a new separation process.

In like manner, the modern day refiner and petrochemical producer has available adsorption separation processes. Specifically, molecular sieve adsorption processes have become a proven means of separating

n-paraffins from other hydrocarbon classes. Today there are over twenty commercial production units in operation utilizing at least six different process schemes.

The Union Carbide IsoSiv Process is one such process which gained early acceptance and has maintained a leading position to the present day. The technology of n-paraffins separation by adsorption had its start in the late 1950's in the separation of n-paraffins from gasoline for octane improvement purposes. The first commercial application was an IsoSiv Process unit installed by South Hampton Co., of Silsbee, Texas, USA. Since that time, six additional adsorption units for separating n-paraffins from naphtha range feedstocks have been installed in the U.S., Germany, Italy and Japan, the most recent having started-up in 1973. They range in size from 10,000 to 55,000 metric tons per year of n-paraffin separation capacity. All such installations have utilized the IsoSiv Process.

During the early 1960's, the appeal of molecular sieve adsorption led to widespread efforts at innovating new adsorption technology. Many of these efforts were successful in that they resulted in molecular sieve processes capable of separating long-chain n-paraffins from kerosine-range feedstocks at just that time when the detergent industry decided to switch to linear alkylbenzene sulfonates as a basis for its formulations for "soft" detergents. The consequent demand for long chain n-paraffins led to a world-wide wave of construction resulting in at least twelve adsorption plants processing kerosine range feedstocks utilizing processes developed by Union Carbide, UOP, Esso, British Petroleum, Shell and Texaco. Among the first was South Hampton Company's naphtha IsoSiv converted to the kerosine range in 1961. In 1964 Union Carbide Corporation installed at its Texas City, Texas, USA petrochemical complex an IsoSiv Unit producing 100,000 metric tons per year of n-paraffins from kerosine. This unit was to remain the world's largest n-paraffin producing plant for almost ten years.

At the beginning of this decade a further extension of adsorption technology has been required. The n-paraffins used as substrate for protein production extend into the gas-oil feedstock range. Suitable modifications can and have been made to the existing adsorption technology to allow successful application to the new requirements. In 1972 Liquichimica S.p.A., a subsidiary of the Liquigas Group of Italy, installed and started-up in Augusta, Sicily, a modified IsoSiv Unit to produce 110,000 metric tons per year of n-paraffins from both kerosine and gas-oil feedstocks. Plant expansions put on-stream in 1973 have brought the n-paraffin production capacity at Augusta up to approximately 250,000 metric tons per year; by a wide margin the largest single n-paraffin producing installation in the world. Liquichimica's IsoSiv Units have utilized feedstocks ranging from kerosine to gas-oil and intermediate mixtures of both.

Liquichimica presently has two additional IsoSiv Units of over 200,000 metric tons per year each under construction for 1974 start-up. These units will also utilize mixtures of kerosine and gas-oil feedstocks. The total installed capacity will then be over 650,000 metric tons per year of n-paraffin production.

The IsoSiv Process (as an example) has adequately demonstrated the commercial viability of molecular sieve adsorption processes as a method to obtain n-paraffins for protein production. Economics of installation and operation and the quality of products are indicated by the wide commercial acceptance of the process (twelve units in operation and two under construction). Processing flexibility (naphtha through gas-oil), production capacity (10,000 to 200,000 metric tons per year) and reliability (almost 15 years of commercial practice) are also clearly evident among the installed IsoSiv Units.



## II. PROCESS DESCRIPTION

### A. General

The IsoSiv Process separates n-paraffins from a hydrocarbon mixture such as kerosine or gas-oil by selective adsorption on a molecular sieve adsorbent material. This material is a crystalline zeolite having very uniform pore dimensions of the same order of magnitude as the size of individual hydrocarbon molecules. The molecular sieve utilized for n-paraffin separation is of the 5 A Type, meaning that the pore openings in the crystalline structure are of about 5 Angstroms in diameter. N-paraffin molecules have average diameters of less than 5 Angstroms and can therefore pass through the pore openings into the internal crystal cavity where they are retained. Non-normal hydrocarbons such as iso-paraffins, naphthenes and aromatics have molecular diameters significantly larger than 5 Angstroms and are therefore excluded from entering the crystal cavity through the 5 Angstrom pore opening.

The heart of the IsoSiv Process is the adsorber section consisting of vessels filled with molecular sieve adsorbent. The kerosene or gas-oil feedstock is fed into one end of an adsorber vessel, the n-paraffins in the feedstock remain in the vessel by being adsorbed in the molecular sieve and the remainder of the feedstock passes out of the other end of the vessel as a de-paraffinated kerosine or gas-oil. In a following process step, the n-paraffins are recovered from the adsorber vessel as a separate product by use of a purge material. All process hardware in an IsoSiv Unit is conventional refinery equipment such as pumps, furnaces, heat exchangers and compressors designed to deliver the feedstock and the purge material to the adsorber section and to remove the products from the adsorber section.

The following more detailed process description and the schematic flowsheet of Figure 1 will explain the utilization of the auxiliary equipment in the process unit as well as give some insight into the occurrences within the adsorber vessels.

### B. Adsorption Step

Hydrocarbon feed at elevated temperature and somewhat above atmospheric pressure is passed upward through one adsorber vessel where the normal paraffins are selectively adsorbed in the bed. In the case of processing gas oil feedstock, hexane is added to the gas oil feed to dilute it and prevent capillary condensation from occurring on the adsorbent bed. As the normal paraffins are adsorbed, the liberated heat of adsorption creates a temperature front which travels through the bed. This front closely coincides with the mass transfer front and gives an indication of when the adsorption step should be terminated to prevent the normal paraffins from breaking through the effluent end of the bed. This temperature front is used in pilot plant work to determine the optimum design conditions, however, in a commercial unit the adsorption step is terminated by a cycle timer set to prevent the front from reaching the bed exit. The unadsorbed isomer and cyclic hydrocarbons that pass through the beds are heat exchanged against the feed stream to recover heat. This stream is then sent to a distillation system where the hexane purge material is recovered as a distillate product and the heavy isomers are taken as bottoms products.

### C. Co-Purge Step

Following the adsorption step, the n-paraffin loaded beds are purged in the cocurrent direction with just enough vaporized hexane to displace the non-adsorbed feed and isomeric hydrocarbons from the void spaces in the adsorber vessel. This step is important in the production of protein substrates since it insures that a high purity product will

be recovered in the desorption step. The effluent from the cocurrent purge step is combined with the adsorption effluent stream. The combined adsorption and cocurrent purge effluent stream is heat exchanged with the cold incoming feed and then sent to the iso-dehexanizer system where the hexane is removed from the heavy isomer product.

#### D. Desorption Purge Step

Following the cocurrent purge step, the beds are purged countercurrently with hexane. This countercurrent purging desorbs the normal paraffins and sweeps these desorbed vapors from the bed thus maintaining the average desorbate partial pressure below the value in equilibrium with the loading on the bed. The continuous removal of the desorbate vapor with the simultaneous transfer of the adsorbed phase to the purge gas in an attempt to establish equilibrium drives the desorption toward completion. In addition to this stripping effect, the normal hexane, itself, becomes adsorbed on the bed and displaces the heavier normal paraffin desorbate. A complete removal of the heavy normal paraffin adsorbate is not achieved on each desorption. An economic balance between the bed size, as determined by the fraction of heavy normal adsorbate removed or "delta loading" and the hexane purge required determines the degree of removal of heavy normals obtained. As the purge quantity is decreased the delta loading is decreased requiring larger adsorbers for a given hydro-carbon feed through-put and cycle time. This decreased delta loading increases the rate of adsorbent deactivation and consequently the required burnoff frequency, because the higher residual loading increases the rate of coke formation. Conversely, increasing the purge quantity increases delta loading until the hexane handling equipment and operating costs become significant factors.

The desorption effluent containing heavy n-paraffins and hexane is partially condensed by heat exchange with the cold hexane feed. The vapor fraction and the condensate are transferred to the normal dehexanizer system where the normal paraffins are separated from the hexane by standard fractionating techniques. The normal paraffin product from the bottom of the column is cooled and removed from the process. This separation is relatively easy due to the wide difference in boiling point between hexane and the lightest heavy normal paraffin. The recovered hexane from this column is also condensed and circulated back to the hexane accumulator without fractionation. Small additions of fresh hexane are required to make up losses of hexane carried out in both product streams.

The foregoing operation sequence is integrated into continuous processing by the cyclic use of several adsorber vessels with automatic valves operated by a sequencing control system. Flow of both feed and products is uninterrupted. Suitable interlocks and alarms are provided so that the plant can operate with a minimum of operator attendance.

#### E. Oxidative Regeneration Description

As the adsorber beds are cycled at the elevated operating temperatures, a carbonaceous deposit gradually accumulates. This deposit reduces the capacity of the adsorbent, which ultimately results in a breakthrough of normal paraffins into the isomer product stream and decreased normal paraffin recovery. The rate at which this deposit accumulates depends on factors such as, temperature, feed impurities, feed properties, cycle time, and residual paraffin loadings. This type of adsorbent deactivation is temporary so that original bed capacity can be restored by burning off this deposit under controlled conditions. For a kerosene type feedstock, a bed can be cycled for

15 to 30 days before oxidative regeneration is necessary. For a gas oil feedstock the period is reduced to about 6 to 10 days.

When a bed has been cycled to the point that oxidative regeneration is required, it is removed from processing operation and another adsorber vessel is put into operation. This change is made without any interruption in the cycling sequence. The coked bed is removed from cycling after the desorption step and is given an additional long desorption purge to remove as much of the residual normal paraffins as possible. The bed is then completely isolated from the cycling system and a countercurrent circulation of nitrogen is established. The nitrogen is pumped by means of a compressor or blower and then passed through a heater to the adsorber vessel. The circulation of hot nitrogen has two purposes: (1) to purge the hexane from the bed, and (2) to raise the temperature of the bed to above the coke ignition point prior to introduction of oxygen into the system. The effluent gas from the bed is cooled to condense the hydrocarbons and water that desorb. When the bed is up to temperature, air is introduced into the circulating stream at a controlled rate. The oxygen in the gas combusts with coke in the top of the bed. The heat released from combustion is carried out of the burning zone as a preheat front travelling ahead of the burning front. This preheat front raises the bed temperature even further. This temperature is controlled by regulating the amount of oxygen in the entering gas. Excessive internal adsorbent temperatures will permanently destroy the molecular sieve crystal so the gas phase temperature is critical. As the burning front passes through the bed the temperature will drop back to the gas inlet temperature. Since the coke deposit contains hydrogen, water is formed during combustion in addition to carbon oxides. This water must be removed from the system because the molecular sieve crystal is permanently damaged by repeated exposure to

water at high temperatures. Driers are used to prevent the water from accumulating, thereby, minimizing this damage. Proper design of the regeneration procedure and the rugged nature of the molecular sieve insure a long operating life of the adsorbent.

After the regeneration is complete, the bed is cooled down to the process operating temperature and purged of any remaining oxygen by circulating nitrogen. The bed is now ready to go on stream to replace one of the adsorbers in use so that it in turn can be reactivated.

### III. APPLICATION RECOMMENDATIONS

The requirements to be met in achieving the optimum design and application of a molecular sieve adsorption unit involve many factors. Among the more important of these factors to be considered are the following:

1. Nature of the feedstock - Of prime importance is the n-paraffin content, the hydrocarbon number range and the amount and type of impurities such as sulfur compounds.
2. Nature of the products - The n-paraffin product purity requirement and the hydrocarbon range and type of individual product cuts is significant.
3. N-paraffin production capacity - Not only is the total production capacity of technical and economic concern, but also the capacity requirements for individual product cuts.
4. Typical engineering requirements - These include the usual items such as availability, cost and conditions of fuel, power and water supplies, climatic conditions, transportation and storage facilities, manpower, etc., all of which influence the design of the operating unit.

For an IsoSiv Process Unit a number of inter-related design parameters must be selected and combined in an effective manner to achieve an optimal degree of satisfaction of all process requirements. Among these are:

1. Operating conditions such as temperature, pressure and cycle time.
2. Flow rates of critical streams such as the purification purge and the desorption purge materials.

3. Use and amount of feed diluent.
4. Frequency and type of oxidative regeneration.
5. Pre- and post fractionation.
6. Pre- and post treatment of feed and product streams.
7. Amount and characteristics of molecular sieve adsorbent to be used.

Although the principle of operation of a molecular sieve adsorption process unit is not difficult to understand and an IsoSiv Process Unit is relatively easy to install and operate, the process design and engineering to achieve optimum results is indeed very complex. It would not be possible here to thoroughly discuss, or even to define and demonstrate, the intricate inter-dependency of the process requirements and design parameters listed here.

However, a number of recommendations for the application of such processes may be set forth based upon the experience gained through the successful implementation of many commercial projects through the combined efforts of the process designer, the engineering contractor and the user-manufacturer.

The three most important of these recommendations are:

1. Large-size - The plant should be designed for as large a production capacity as possible within technical and economic considerations. Plants below 100,000 mta are considered to be relatively small in size from an economic point of view. The 250,000 mta plant lies somewhere in the middle of the preferred range and plants larger than 500,000 mta offer little economic incentive.
2. Processing flexibility - The plant should be designed to produce a variety of n-paraffin products from readily available feedstock sources.



Feedstock mixtures (such as kerosine and gas-oil together) are preferred because the use of such mixtures improves the operating economics of the plant and also allows the combining of several product requirements to utilize a larger single plant size.

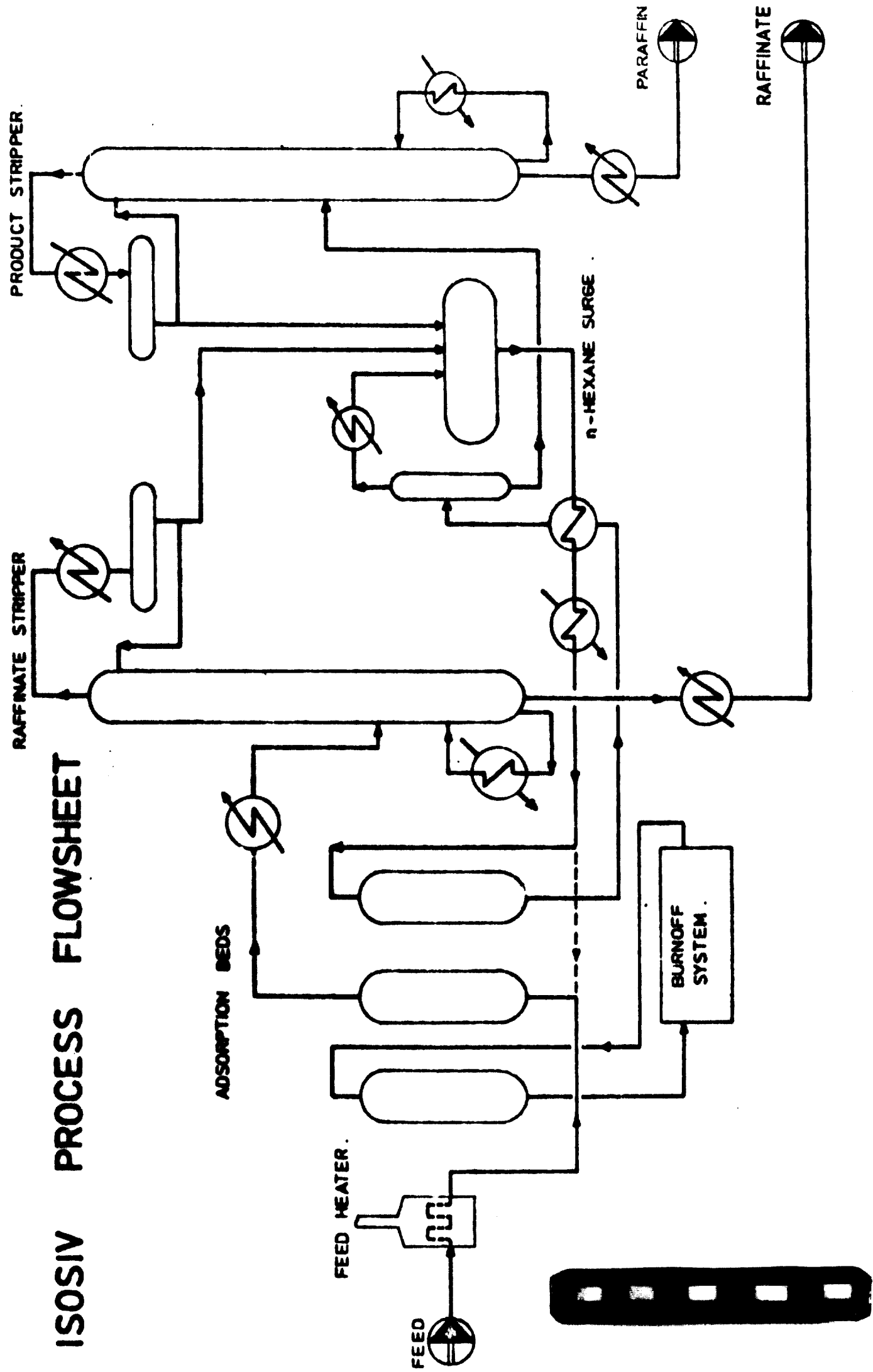
3. Requirements coordination - A high degree of coordination and a maximum of cooperation must be exercised between the adsorbent manufacturer, the process designer, the engineer-contractor and the user-manufacturer in order to obtain the maximum benefit of the experience, abilities and capabilities of the individual contributors to a successful project.

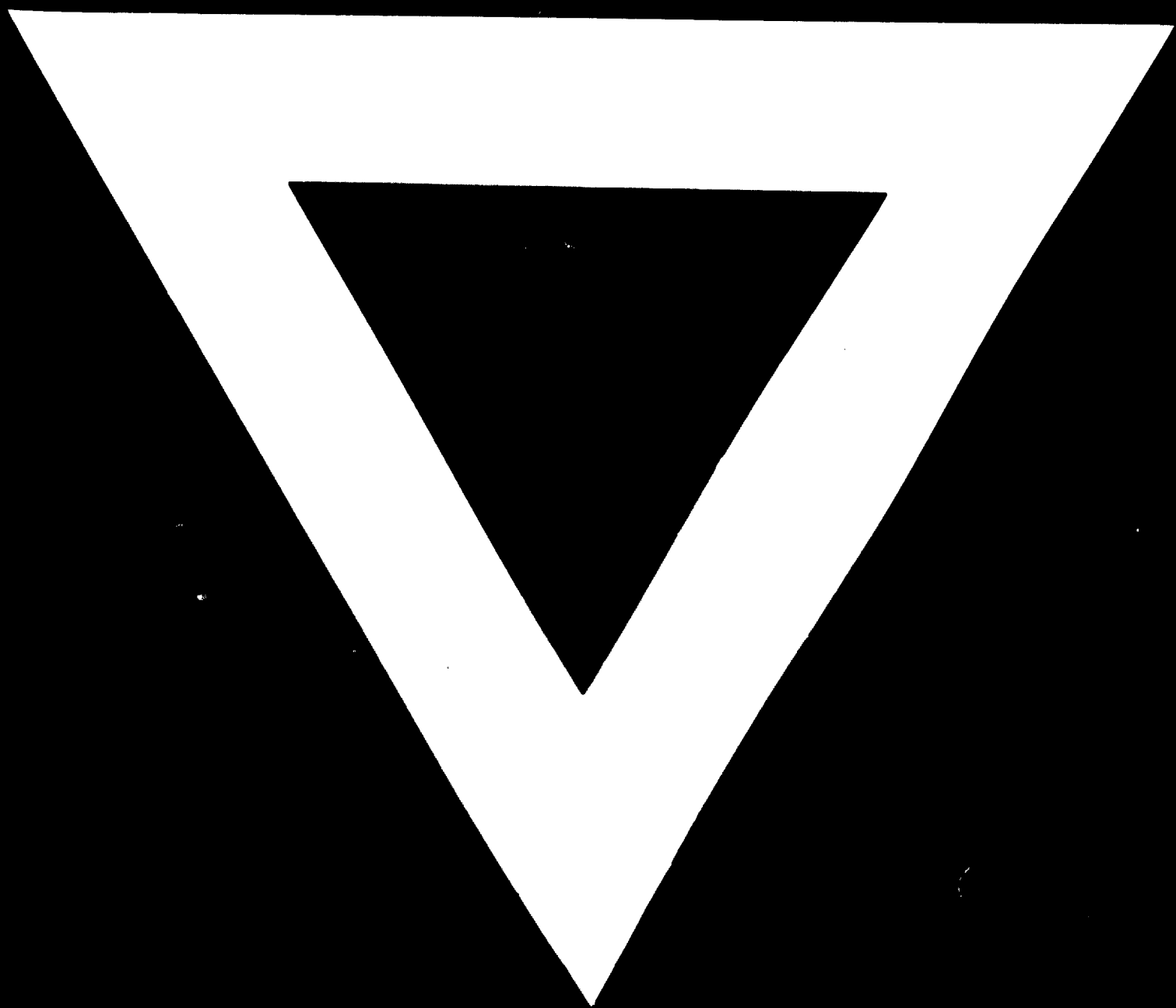
In summary, commercially proven large scale production technology is available today for the economic production of high quality n-paraffins to be used as substrate for the production of single cell protein. This technology can presently be best applied through the careful integration of several industries to obtain centralized production and optimized usage of a wide range of n-paraffin products.

IV. ACKNOWLEDGEMENT

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# ISOSIV PROCESS FLOWSHEET





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