A Decision Tree for Technology Selection of Nitrogen Production Plants

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Abstract

Nitrogen is produced mainly from its most abundant source, the air, using three processes: membrane, pressure swing adsorption (PSA) and cryogenic. The most common method for evaluating a process is using the selection diagrams based on feasibility studies. Since the selection diagrams are presented by different companies, they are biased, and provide unsimilar and even controversial results. In order to provide an impartial evaluation means and getting an integrated and reliable selection method, all existing diagrams have been reviewed in this paper and integrated into a single diagram. With the help of proposed selection diagram and considering the operating conditions, flow rate and purity of Nitrogen, the most economic technology for separation of Nitrogen from the air can be chosen. Of course for some values of purity and flow rate, more than one technology can be selected. In these ranges, other parameters such as economic value of by-products phase of delivered product fluid (liquid or gaseous) and the product applications should be taken into account.

In order to provide an engineering tool for selecting the most economic technology of Nitrogen production, a decision tree is proposed. With this decision tree one can choose the most suitable technology for its production. Heuristic rules along with literature data are implemented within the decision tree and it has been validated and updated with domestic Nitrogen producing companies. Generally for high capacity of Nitrogen production, the cryogenic process is the most economical alternative and for medium and low capacities, PSA and membrane systems are the best choices, respectively. Finally, a computer program is proposed to find out the most suitable technology for Nitrogen production.

Keywords: Separation, Nitrogen, Membrane process, Pressure swing adsorption, Cryogenic process

Introduction

Nitrogen (N_2) is an industrial gas with numerous applications: ammonia production, safety blanket gas for inflammable material storage tanks, replacing air for storage, packaging and freezing of food products and as refrigerant in cryogenic cycles. In the chemical process industry, N_2 is applied as an inert material in chemical reactors and also as corrosion preventer in pipe lines. N_2 is injected into oil and gas reservoirs [1] for pressure buildup in Enhanced Oil Recovery (EOR) operation.

The main criteria for choosing suitable process of air separation are: selection between O_2 or N_2 as the main product, process operating conditions (flow rate, high or low pressure, desired phase of product (gas or liquid)), purity of product, and energy cost. To provide an engineering tool for selecting among these criteria a decision tree is proposed in this paper, after investigating different processes of N_2 separation from the air. Usually the application dictates the purity of the product, for example the blanket inert of N_2 does not tolerate ppm scale presence of O_2.

1- N_2 separation processes from the air

There are three main N_2 purification methods for separation of N_2 from air: Pressure Swing Adsorption (PSA), membrane separation, and cryogenic process.

1-1- Pressure swing adsorption process

In this process air is flown alternately on two beds of adsorbent material. A simplified flow diagram for the PSA process is shown

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in Fig. (1) Air stream (S1) at ambient conditions (T = 25 °C, P =1 bar) is fed to the compressor (C1). The compressor increases the air pressure up to 8 bar. The outlet air stream from compressor (S2) is sent to the adsorbent bed (CMS#1) operating at high pressure. Different adsorbents are used such as zeolite and alumina. The upper part of the bed removes all of the water content and CO_2 that were initially present in the air. When the composition of the O_2 in the effluent begins to approach the specified value of 1% (which occurs as the bed becomes saturated) the break point is reached. At this point, the inlet flow (S2) is diverted to the other adsorbent bed (CMS#2) and at the same time the pressure of first adsorption bed (CMS #1) is decreased for desorption operation [2].

After saturation of the second bed, inlet stream is sent to the first bed (CMS#1), again. In this section O_2 (S4) is separated by adsorbent beds (CMS#1) and (CMS#2) and is sent to the Silencer (SL1). The purity of N_2 in outlet stream (S3) obtained from each bed, is more than %97 at 25 °C and 7.9 bar [2].

1-2- Membrane system

With development of membrane technology, this process witnessed a rapid growth. A suitable membrane is used to separate N_2. A simple flow diagram of the membrane process is shown in Fig. (2) Air (S1) at ambient conditions (T = 25 °C, P =1 bar) is fed to the compressor (C1), where its pressure increases up to 8 bar. Compressor outlet stream (S2) is sent to multiple modules membrane system. Two outlet streams from membrane system are N_2-rich stream (S4) at 25 °C and 7.9 bar and O_2-rich stream (S3) [2].

1-3- Cryogenic process

The conventional process for N_2 production is the cryogenic process which had no major improvement during last decades. The flow sheet, shown in Fig. (3) details this process. The feed to the system (S1) is ambient air at 25°C and 1 bar. A compressor (C1) increases air pressure to 12 bar and then impurities of outlet stream (S2) are removed by Temperature Swing Adsorption (TSA). The TSA bed contains both alumina beads to remove water and Zeolite molecular sieve to remove carbon dioxide. When the air stream (S3) leaves the TSA, it is assumed that it contains no water, carbon dioxide or hydrocarbons. After being cooled in the main heat exchanger (E1), the feed (S4) enters the tray 15 of the distillation column (T1). The vapor product from the overhead condenser contains 99% nitrogen (S11).

The O_2-rich liquid stream (S5) from the bottom of the column provides the cooling for the condenser (E2) once it is adiabatically flashed (as stream S6) through a valve (V1) with a pressure drop of 3bar. The O2-rich waste stream (S7) as a cold stream is sent to the heat exchanger (E1) [3]. A four-cell cryogenic heat exchanger (E1) is used to cool the product with waste streams. The cold streams in the main heat exchanger are the product N_2 (S11) and the O_2-rich waste stream (S7).

The waste stream passes through this heat exchanger as a cold stream twice: once before heat exchanger (S7) and next in the turbo expander (EX1) tagged as streams (S9) and (S10) [3].

The expansion cycle is included in the process to make it more energy efficient. After the waste stream (S6) condenses the N_2 product in (E2), it enters the main heat exchanger as (S7) where it is warmed by the feed air (S3). The stream is then expanded to atmospheric pressure. The outlet O_2-rich stream (S10) can then be used to regenerate the TSA membrane beds [3]. The recovered work by the turbine can compensate part of the feed compressor shaft work. N_2 stream outlet from top of distillation tower (S11) is sent to heat exchanger (E1) and a valve (V2) with a final outlet pressure of 7 bar [3].

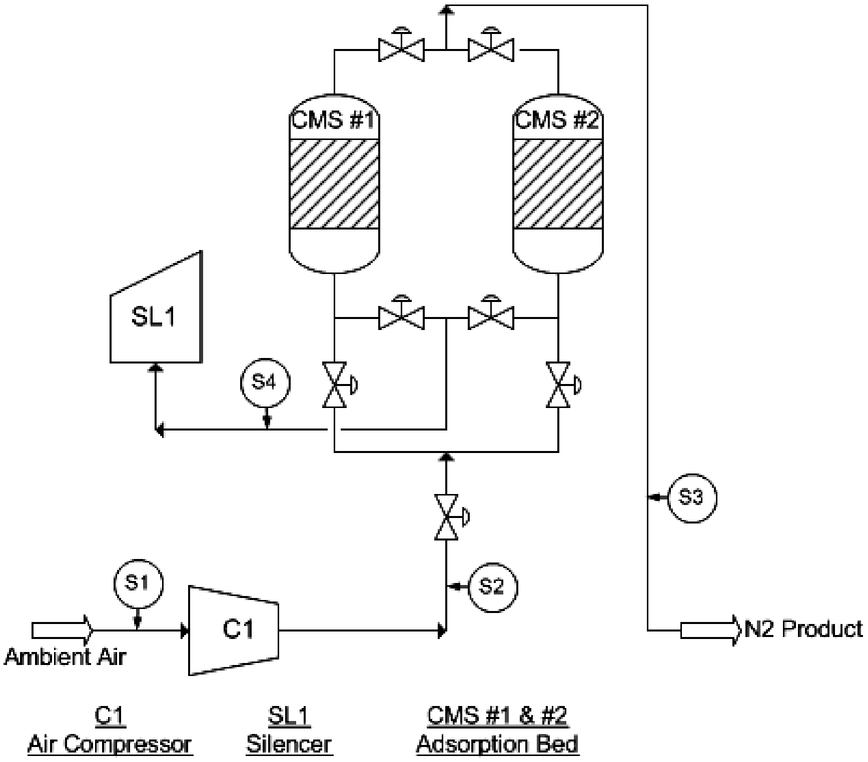

Figure1: Simplified flow sheet of PSA Process

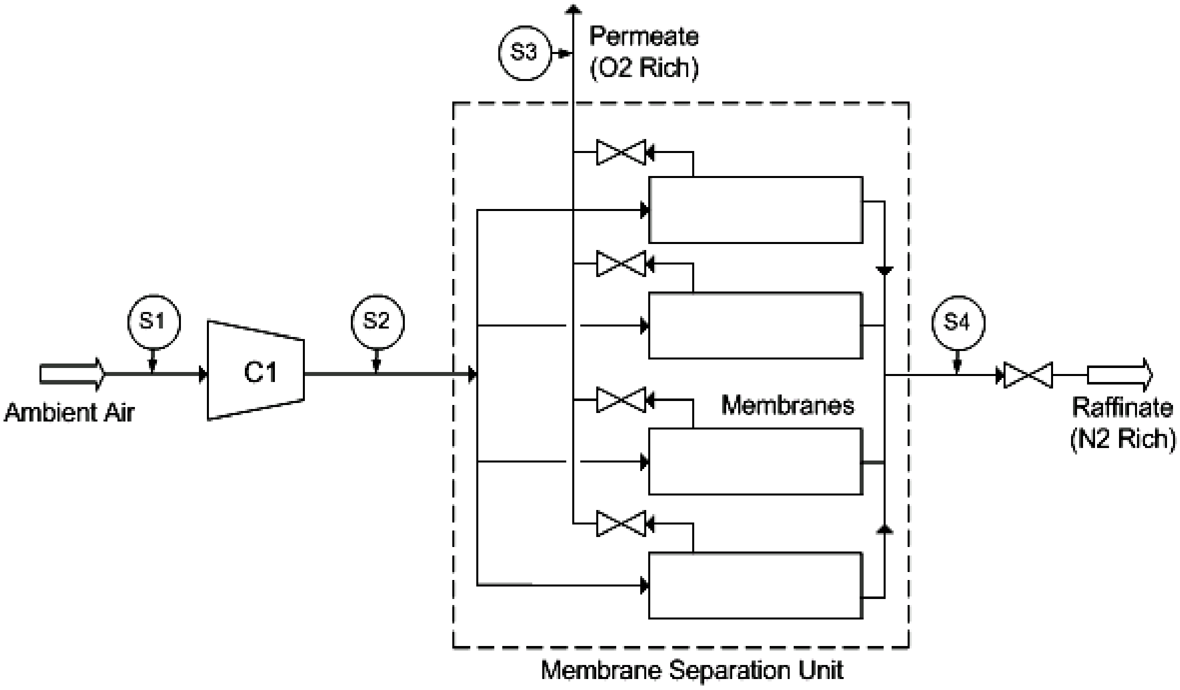

Figure 2: Flow sheet of membrane system

2- Advantages and disadvantages of N_2 separation processes from air

In general, the N_2 separation processes from air can be divided into two groups of non-cryogenic and cryogenic type. The description of these processes will help the reader to find out the most suitable selection for his own purpose, when evaluating their advantages and disadvantages.

2-1- Non-cryogenic processes

Non cryogenic processes operate at ambient temperature and medium pressure based on physical adsorption. These systems are commercialized for small scales, low flow rate and medium purity of N_2 and when only one product (N_2 or O_2) is desired [4].

2-1-1- PSA

PSA system operation is based on physical adsorption of O_2 over adsorbent materials which are usually active carbon, alumina and zeolite. For N_2 production, only active carbon and zeolite (4A) are used [5].

In this system, air initially passes through the first adsorbing bed where O_2 is adsorbed and N_2 pass through as product. PSA process advantages are a follows [6]:

- If the amount of N_2 needed is less than 560 m^3/hr (20,000 SCFH), selecting a PSA process is more economical than a cryogenic process.
- During the shutdown period, the loss of profit is less than cryogenic processes.
- PSA units are readily available and can be purchased and delivered quickly.

Disadvantages of PSA process can be summarized as [6]:

- If the flow rate is increased to 1120 m^3/hr (40,000 SCFH), it becomes significantly cheaper to produce N_2 from a cryogenic process.
- There is a possible down time for repair or maintenance of the compressor.
- Extremely noisy when compared with other processes.

2-1-2- Membrane process

Membrane process, adopted for air separation since the 1980's, uses the selective permeability of the hollow-fiber polymeric membranes to separate the N_2 from the O_2 as a result of the pressure difference. Nowadays, the membranes are made of polysulfones, polyimides and polycarbonates [7].

Membrane process is the optimal commercial method for N_2 production at low capacity with purity of %99.5 and O_2 with purity 0f 30-50% as a by-product; but at higher production capacity, cryogenic process must be selected [8]. Some of advantages of membrane systems are [1]:

- light weight
- zero maintenance cost
- wide range of working temperature
- mobility

However, membrane processes are not suitable for high pressure applications.

2-2- Cryogenic process

One of the current N_2 separation processes from the air is the cryogenic process which became commercial at early twenty century. Cryogenic process uses distillation towers that operate at very low temperatures (at about -170 °C and thus sometimes called cold box process) and pressure of 8 -10 atm in which the air starts to liquefy [9].

The advantages of cryogenic process are [9]:

- It can produce large quantities of high-purity N_2.
- Cryogenic processes do not have economics of scale i.e., increase or decrease of plant capacity generally does not necessitate new equipment.

Cryogenic process disadvantages are [9]:

- It requires compressor and turbine which increase the capital investment and maintenance costs.
- Cryogenic plant needs large land so this process is not suitable for restricted surface area.
- Liquid N_2 production is an energy-intensive process. Currently practical refrigeration plants producing a few tons/day of liquid N_2 which operate at about 50% of Carnot efficiency.

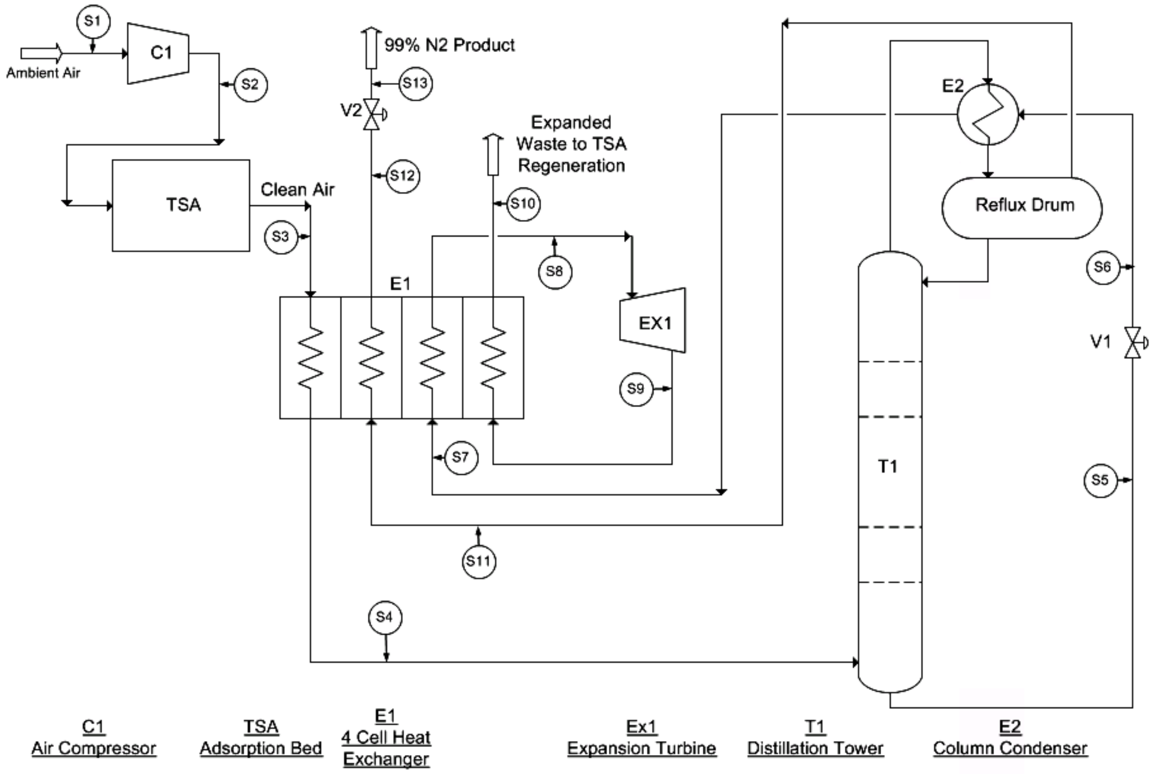

Figure 3: Simplified flow diagram of cryogenic process

Table 1: Comparison of N_2 separation methods

Process	**System complexity**	**Process flexibility**	**Mobility**	**Product and purity**	**Capacity**
PSA	Complex	Low	Pretty possible	One stream (99%)	Average
Membrane	Simple	Low	Possible	One stream (+99%)	Low
Cryogenic	Complex	Low	Impossible	Two streams (impurity ppm)	High

2-3- Comparison of three methods for N_2 separation

Air components can be separated by three methods: PSA, membrane and cryogenic systems. Table (1) depicts a brief comparison of the mentioned methods.

N_2 or O_2 price depends only on capital, operating and transportation costs because of being independent of the raw material.

Membrane system has low operating cost therefore this process can compete with other air separation processes. Today’s membranes are more permeable for O_2, CO_2 and H_2O than N_2, so the waste stream is rich of N_2. The purity of N_2 produced by membrane process systems exceeds 95 to 99.5% [1].

Cryogenic processes need large surface area and they are not suitable for pressures higher than 10 atm. They are able to produce high purity N_2, but at small scale do not have a high efficiency [9].

The production cost elements of these processes (PSA, membrane and cryogenic) are shown in detail in the pie-charts of Fig. (4) to 6.

When selecting a suitable process several parameters should be considered, among which purity and capacity are the most important. The other parameter is the pressure of delivered product to customer which determines the phase of product (liquid or gas).

3- Selecting a suitable process

- Commercial importance of by-product: when the by-products such as O_2 or argon have economic value, the cryogenic process is more attractive than PSA or membrane.
- Kind of product application: continuous production for process operation or cylinder filling.

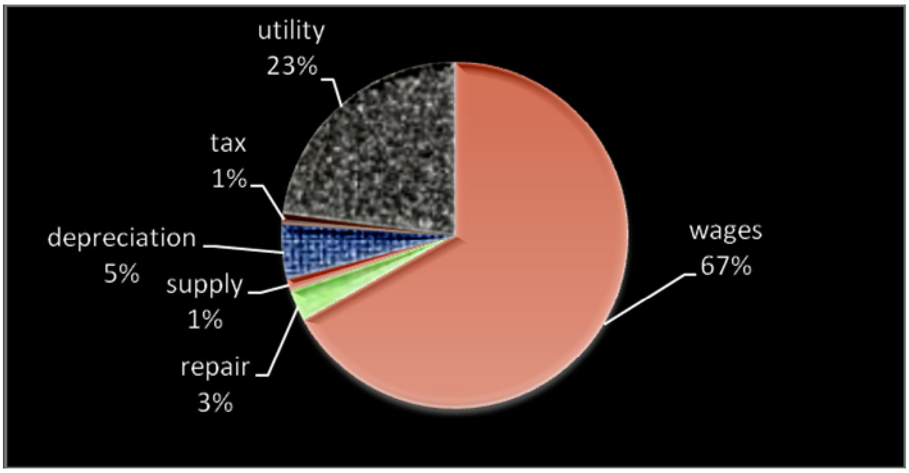

Figure 4: PSA process production cost breakdown [2]

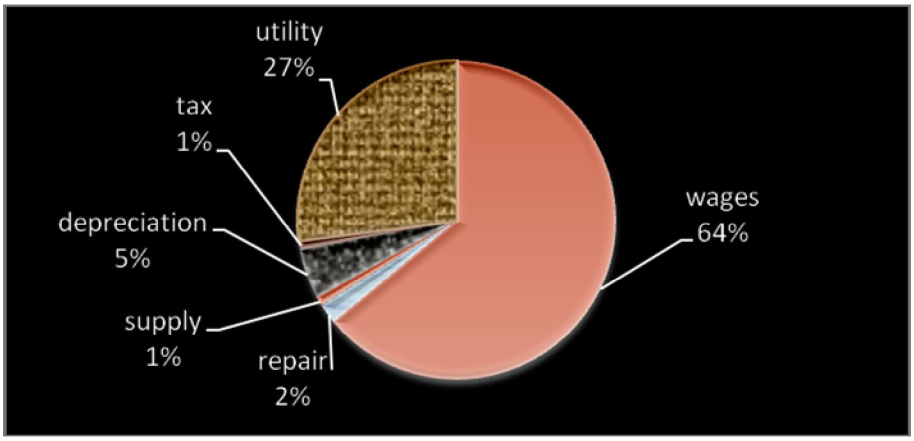

Figure 5: Membrane process production cost breakdown [2]

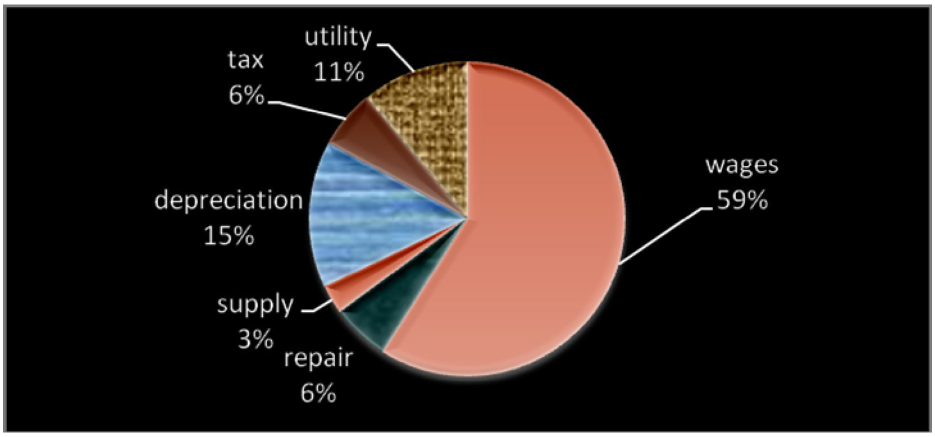

Figure 6: Cryogenic process production cost breakdown [3]

There are many methods for evaluating a process; the most common one is the feasibility study which leads to the selection diagrams of figures (7) and (8) [10, 11]. Succinctly, two of these selection diagrams are presented here but the interested reader may consult other references [5, 7] as well. These figures are based on two most important parameters: N_2 purity and its flow rate. Because of technological and technical improvements in air separation methods, these figures will change over time and place.

As these graphs are offered by different companies, they do not provide similar results. For example for a specific purity and flow rate, one may suggest the membrane system as the most economic choice while the other presents PSA process as the best one. In order to provide an impartial evaluation means and getting an integrated and reliable selection method, all existing figures have been reviewed. The literature data and figures were digitized and then integrated to provide a single curve, shown in Fig. (9). Since the literature diagrams (Figures (7) and (8)) has been reported by non-Iranian companies, the mentioned graphs has been updated and validated based on domestic N_2 producers advices and some of the utility units of Bandar-e-Imam and Assalouyeh, in southern Iran.

Considering Fig. (9), it is obvious that for high capacity and high purity of N2, the cryogenic process is the most economical method compared to the other ones. However, for medium capacity and high N_2 purity, PSA process is the best choice and for low capacity, the membrane system is the most appropriate process. Of course at the border lines, where multiple choices exist, it is better to choose the suitable air separation process based on other parameters like economic value of by-products.

3-1- Decision tree

As it is already said, with the help of Figure (9), the most economic technology for N_2 separation can be chosen. In the case that more than one technology can be selected, other parameters such as economic value of by-products should be taken into account. So, with investigating the advantages and disadvantages of technologies and considering other parameters, a decision tree is presented by which the user can easily choose the suitable technology for N_2 production.

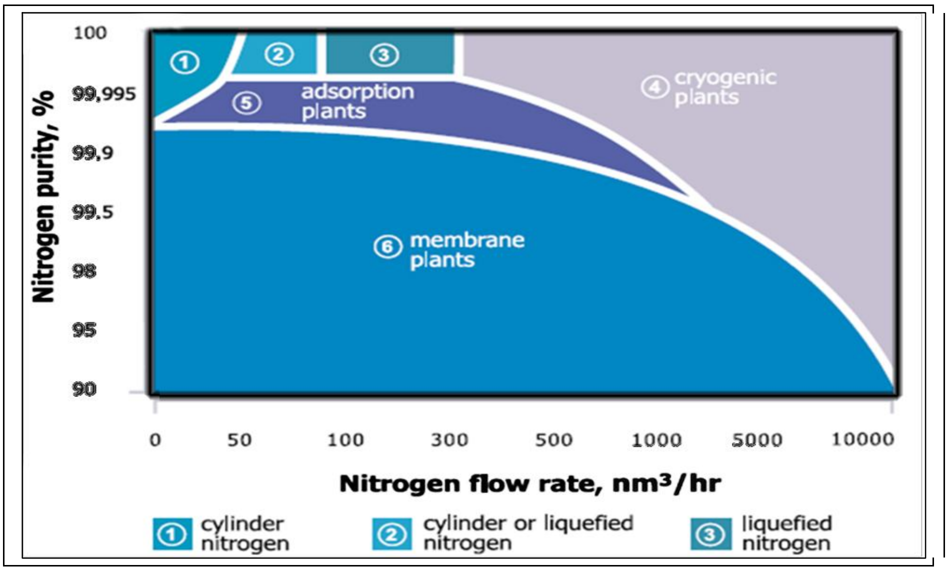

Figure7: Selection Diagram for N_2 production process (2003-2007) [10]

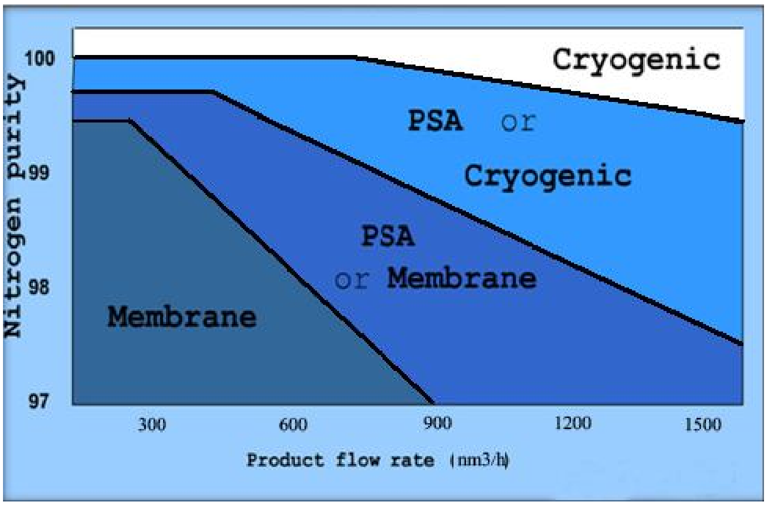

Figure8: Selection Diagram for N_2 production process (2008) [11]

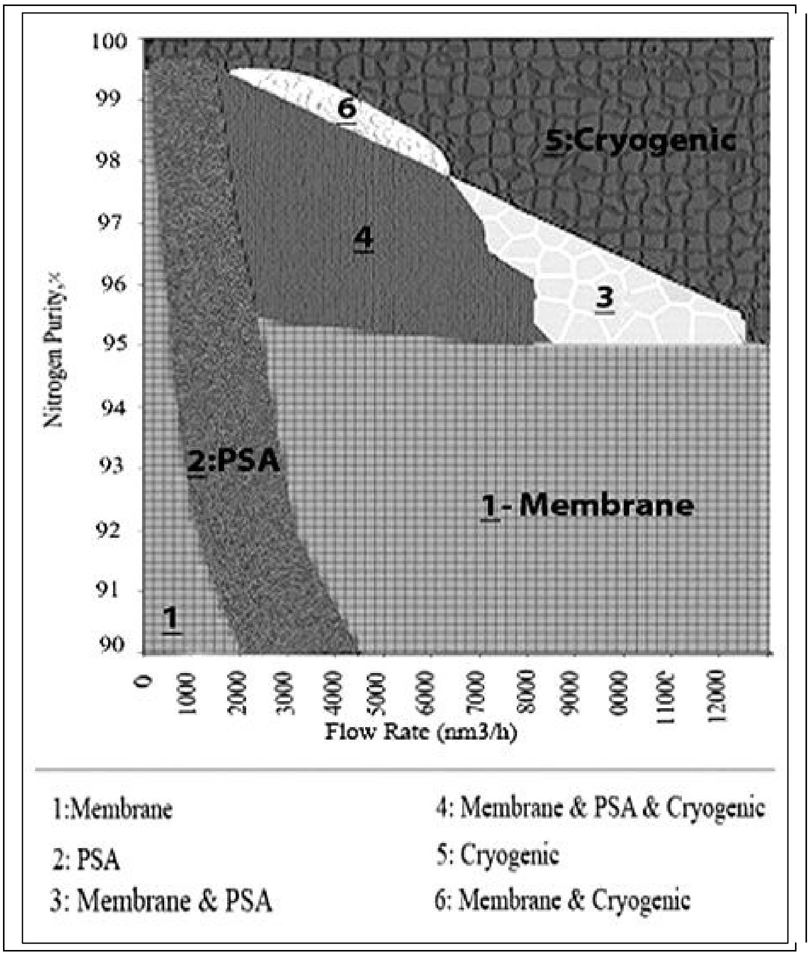

Figure 9: Process selection Diagram for N_2 production technology

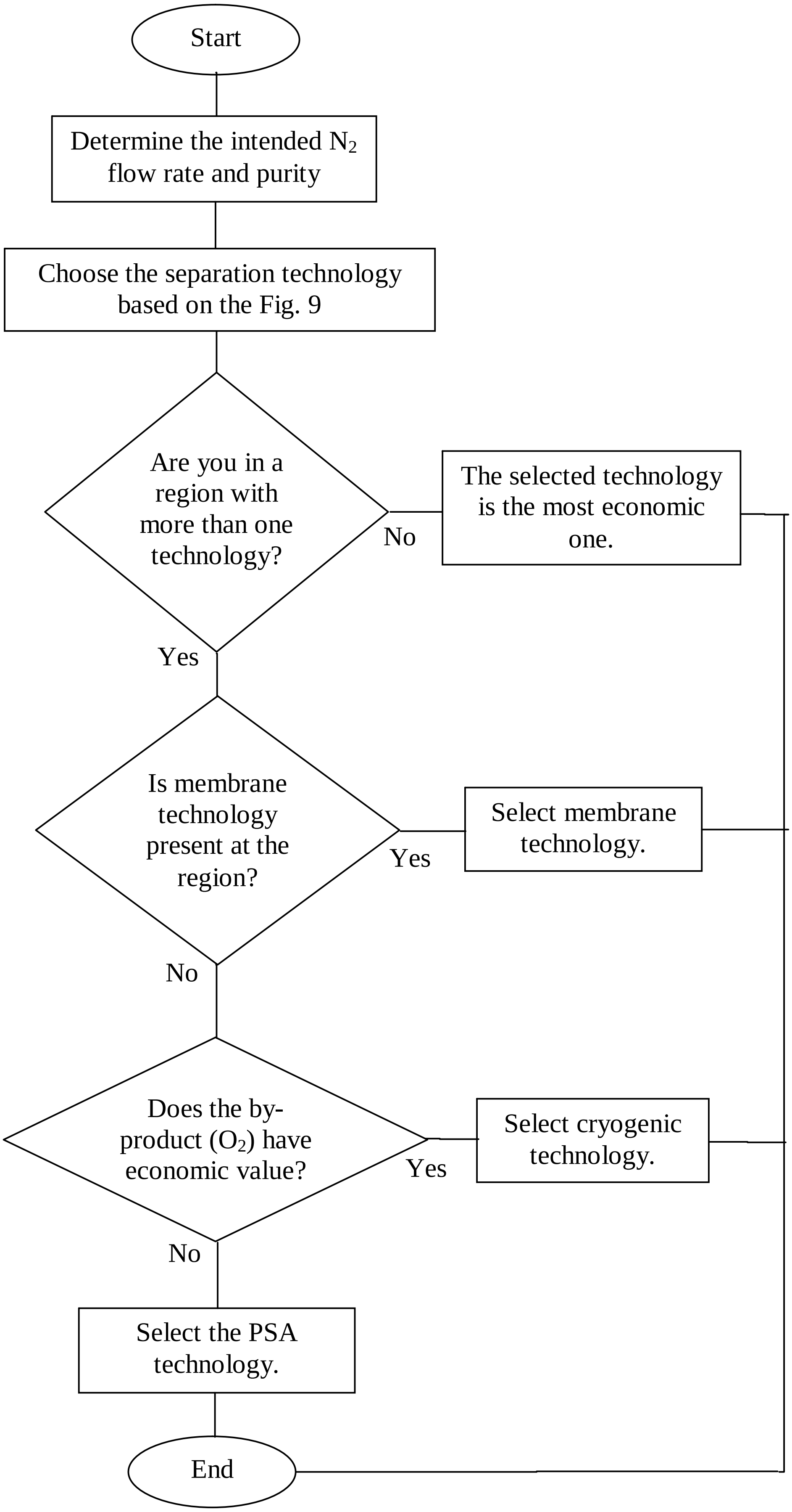

Figure 10 :Decision tree for selecting the best technology of N_2 separation from the air

For proposing this decision tree (Figure 10), following rules have been derived based on advantages and disadvantages of technologies:

1. The cryogenic process has no priority unless a logical reason exists for its selection.
2. The membrane process is in priority relative to other technologies because of its simplicity and near-zero maintenance, unless a logical reason exists for its disqualification.
3. If the O_2 as by-product has an economic value (i.e. it can be sold to a customer), the cryogenic process has the priority because it can produce high purity O_2 as well.

Finally, for user guidance a computer program in MATLAB is proposed to find out the most suitable technology for N_2 production based on intended N_2 flow rate and purity.

4- Conclusion

N_2 has numerous applications in industry. The conventional method for N_2 production is its separation from the air through three different technologies: membrane, pressure swing adsorption and cryogenic. The most economical technology is selected based on the operational conditions (N_2 purity and flow rate). Besides operating conditions, other parameters such as the economic value of by-products, phase of delivered product fluid (liquid or gaseous) and the type of product applications (continuous or intermittent delivery) should also be taken into account. In this paper, these three technologies are investigated based on their advantages and disadvantages.

Generally for high capacity of N_2 production, the cryogenic process is the most economical alternative and for medium and low capacities, PSA and membrane systems are the best choices respectively. Finally, with the help of proposed decision tree and developed program, one can find out the most suitable technology for N_2 production for its own application.

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