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ENERGY FOOTPRINT REDUCTION FOR ETHYLENE MANUFACTURING PROCESS REPORT NO. 8 OCTOBER 2014 PROGRESS REPORT

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1.0 Executive Summary

NOVA Chemicals has undertaken a research and development project focused on adsorptive separation technology in two applications relevant to ethylene manufacturing in Alberta. This project is partly funded by the Climate Change Emissions Management Corporation (CCEMC). The goal of the project is to reduce the energy and greenhouse gas (GHG) intensities associated with separating ethylene/ethane and ethane/methane.

This progress report details the results of experimental, modeling, and design efforts conducted both internally and externally. An adsorption cycle design for ethane/methane separation is presented and the feasibility of implementing the cycle is discussed. The pressure swing adsorption (PSA) cycle could recover 87% of the ethane present in the residue gas stream with 86% purity. Hybridization of the natural gas liquid (NGL) extraction plant with a PSA unit, however, is projected to result in an overall separation system that is not energy efficient. For this reason, as well as due to the significant capital and operating cost associated with hybrid system, it is clear that this technology is not enabling and the Project Team recommends closing out this application.

This update will focus on the development of ethane/methane adsorption technology. Experimental results, the hybrid simulation, and the economic and GHG impact analysis are presented.

This is the last report that will be issued to CCEMC. During the current reporting period, the experimental program focused on adsorption cycle design at the University of Alberta through an NSERC Engage Plus Grant with Dr. Arvind Rajendran. The PSA cycle has been designed through this engagement and the results of the Engage Plus Grant are included in this report. Also presented are the results of the optimized hybrid GSP-PSA which was simulated by NOVA Chemicals using Aspen Plus®. Since this technology was not breakthrough, the technology definition package will not be prepared as was expected by the end of 2014.

2.0 Introduction

NOVA Chemicals operates one of the world's largest ethylene manufacturing facilities in Joffre, Alberta, with annual production exceeding 2 million tons. The process converts ethane to ethylene at high temperature through steam cracking. Throughout this process, beginning with ethane extraction from natural gas and ending with purification of the ethylene product (C2

splitting), the workhorse separation technology is cryogenic distillation. While this technology is ideally suited to the task from a performance perspective, it requires large amounts of energy and contributes significantly to the greenhouse gas (GHG) emissions from ethylene manufacturing.

Ethane, the main feedstock of ethylene manufacturing, is primarily produced through separation from a natural gas stream at cryogenic temperatures. The most frequently utilized technology for this purpose is the Gas Subcooled Process (GSP). The core of this process is a cryogenic distillation column known as the demethanizer. Distillation is a high energy intensity process because a two-phase mixture is needed for separation. In a typical application, natural gas at approximately 5000 kPa and 4 °C is expanded to 2000 kPa and temperatures approaching -100 °C. The ethane and other natural gas liquids (NGLs) are recovered at the bottom of the column. The overhead gas product of the column, termed residue gas, contains primarily methane and must be recompressed before it is returned to the pipeline for distribution to customers as fuel. The power required to recompress the residue gas plays a major role in the economics of NGL recovery.

The process of cracking ethane to manufacture ethylene operates under equally extreme conditions. At the front end of the plant, ethane is cracked at approximately 840 °C and 150 kPa to produce ethylene. The ethylene is then separated from ethane in the final stage of the process at temperatures between -40 °C and -15 °C and pressures near 1500 kPa, as required to form a two-phase mixture in the C2 splitter. The energy required to cool the cracked gas and drive the C2 splitter process is supplied by a propylene refrigerant compressor, which represents a significant fraction of the total GHG emissions from NOVA Chemicals' ethylene plants.

While well-developed and technologically mature, cryogenic distillation is but one of a number of separation technologies which could be applied to ethane recovery and ethylene manufacturing. Recent developments in molecular sieve technology may offer a breakthrough which could improve the energy efficiency of such separation through a process known as adsorption. Adsorption is defined as the adhesion of molecules from a gas or liquid phase onto a solid surface; when one component of a mixture binds more strongly with the adsorbent than the other components, selective separation can be achieved without the need to form a two-phase mixture.

Through sponsorship of the NSERC Industrial Research Chair in New Micro-porous Molecular Sieves at the University of Alberta, NOVA Chemicals has been working with Dr. Steven Kuznicki to develop novel zeolite adsorbents for ethylene/ethane and ethane/methane separations. Zeolites are a special class of molecular sieve with a highly crystalline structure and narrow pore size distribution into which certain molecules may enter. NOVA Chemicals has also initiated a second partnership at the University of Alberta with Dr. Arvind Rajendran, through the form of an NSERC Engage Grant and NSERC Engage Plus Grant. Dr. Rajendran has been working on adsorption cycle design for ethane/methane separation. If such adsorptive separations could be implemented, the associated reductions in energy consumption and GHG emissions might be significant.

2.1 Energy Footprint Reduction for Ethylene Manufacturing Process Project Details

Through joint funding from the Climate Change Emissions Management Corporation (CCEMC) and NOVA Chemicals, NOVA Chemicals is investigating the feasibility of energy savings through the application of adsorption technology to ethylene/ethane (Application 1) and ethane/methane (Application 2) separations. Under this project, the possibility of reducing energy consumption and/or GHG emissions associated with these two applications is investigated. The scope of work consists of basic laboratory research and development through process simulation and scale-up analysis, with the aim of developing a technology definition package describing the utility of each of these applications to the NOVA Chemicals ethylene manufacturing process in Alberta.

2.1.1 Application 1: Ethylene/Ethane

At the heart of each of NOVA Chemicals' ethylene plants there is a C2 splitter; the largest of the distillation columns in the plant. These columns separate ethylene product from unconverted ethane. Ethylene and ethane have similar volatility and form a 'close-boiling' mixture, therefore, separating these chemicals by distillation involves large energy input. The successful development of an adsorptive ethylene/ethane separation technology may offer significant reductions in energy consumption and corresponding GHG intensities by supplementing the operation of the C2 splitter.

2.1.2 Application 2: Ethane/Methane

In the initial stage of the project, a number of other separations within the NOVA Chemicals ethylene manufacturing process were considered for adsorption application [1]. This

consideration investigated the potential energy efficiency improvement. Following a review of process conditions and consultations with experts in ethylene manufacturing and zeolite adsorption, an evaluation of applying molecular sieve adsorption to each separation was conducted. Adsorptive ethane/methane separation was selected, as the development of this technology would be of benefit to NOVA Chemicals through improved access to both ethane feedstock and to other NGL extraction operations in the Province of Alberta.

3.0 Goals Planned for Reporting Period

3.1 Application 1: Ethylene/Ethane

Work on Application 1 has been brought to a close [2], with research efforts being focused on Application 2. The current report will focus on the progress made for Application 2.

3.2 Application 2: Ethane/Methane

With respect to Application 2, the milestone for this reporting period was to prepare a technology definition package consisting of an optimized hybrid GSP-PSA simulation model, an economic analysis, and recommendations. The current report includes all of these items. The technology, however, was not viable from economic and environmental perspectives, and therefore, the whole technology definition package did not require preparation. The major components are presented in following sections. In addition, this report includes the results from the work associated with the Engage Plus Grant at the University of Alberta, targeting PSA cycle design with the production of ethane at high purity and recovery.

4.0 Goals Achieved in the Reporting Period

4.1 Communication with Steering Committee

A CCEMC update meeting with Katherine Wilson (Director, Programs, Alberta Innovates-Energy and Environmental Solutions) was held in September 2014 to present final project updates, introduce project resourcing changes, and discuss final recommendations.

In addition, the project team met with the Steering Committee in September 2014. During this meeting, the project team described the progress in adsorption cycle design, hybrid system modeling, and economic analysis. It has been decided to close out this application due to economic infeasibility. The Engage Plus Grant, however, was still ongoing and should have been completed by end of October, 2014.

4.2 Communication with Decision Board

A project update was held with the NOVA Chemicals Petrochemicals Decision Board in October 2014. A presentation was given which covers the conclusions, recommendations, close out for the project, optimized hybrid GSP-PSA system and economic analysis by NOVA Chemicals, and a summary of the adsorption cycle design by the University of Alberta.

4.3 NSERC Engage Plus Grant Update

An NSERC Engage Plus Grant for a collaborative study between NOVA Chemicals and Dr. Arvind Rajendran at the University of Alberta was completed in October 2014. In this reporting period, two face-to-face meetings and two conference calls were held.

The first objective of the study, from April to October 2014, was to design adsorption processes for the extraction of ethane from the residue gas stream targeting high purity and recovery in the C2 stream with relatively low energy consumption. The study also focused on identifying the optimal position of the PSA process within the GSP and on exploring its effect on purity and recovery of ethane in the C2 stream. The final objective was to select the most efficient adsorbent in terms of purity, recovery, and productivity among the three adsorbents selected (Na-ETS-10, ZSM-5/Silicalite, and 13X/Siliporite G5) for the PSA cycle.

As described in the May 2014 report [3], the process constraints were identified by NOVA Chemicals using process simulation. These were then incorporated into the cycle design. Most of the process constraints were related to energy consumption. In particular, a crucial restriction for the cycle design required that the entire light product stream must leave the adsorption cycle at high pressure conditions. In the previous cycle design (Engage Grant), the high purity C2 stream was achieved by removing C1 through a counter-current blowdown from high pressure (HP) to an intermediate pressure (IP). The light product stream required further recompression work to be merged at pipeline conditions (Figure 1a). During the Engage Plus Grant, a new cycle (Figure 1b) was developed in order to remove C1 from the bed while maintaining high pressure conditions. Additionally, a more realistic value for C2 molar fraction in the residue gas was considered in the design by decreasing this value from 2.4% to 1.0%.

To address the design issues, a PSA cycle (Figure 1b) with heavy reflux (HR) at high pressure (HP) and pressure equalization (PE) was designed. Removal of light components using a rich stream of the heavy component was found to be a reasonable option. The C2 rich stream was recompressed up to the pressure level of the adsorption step and a fraction was recycled to the

column in order to push C1 from the bed by means of competitive adsorption. Additional C1 removal from the bed was achieved by means of a pressure equalization step (PE). Thus, the new cycle included:

i) an adsorption step at high pressure, HP = 2400 kPa

ii) a heavy reflux step at high pressure (HP)

iii) a pressure equalization step going from HP to an intermediate pressure (IP)

iv) a countercurrent blowdown (evacuation) at low pressure, LP = 10 kPa

v) a light product pressurization step to restore pressure conditions in the column to 2400 kPa

The PSA cycle also has been simulated using MATLAB code. The simulated profiles of C1 and C2 concentrations along the column at the end of each cycle step are shown in Figure 2b, c, and d for a given operating condition (Figure 2a). C1 and C2 adsorbate concentrations showed moderate and essentially flat profiles along the column length. At the end of the heavy reflux step, C2 concentration increased dramatically as the C2 rich stream penetrated half of the column. At this point, C1 was competitively displaced from the adsorbent bed by the C2 rich stream. During the next step, the blowdown effect achieved by pressure equalization helped to distribute C2 along the bed and thus removed additional C1 from the column. Then, a significant C2 fraction was extracted from the column during the evacuation step. At the operating conditions shown in Figure 2a, the cycle provided a C2 recovery of ~87 % and C2 purity of ~86 % with a productivity of ~0.3 mol/m^3.s corresponding to a cycle duration of 2.9 min.

The increase in feed temperature produced an enhancement of the cycle performance in terms of purity and recovery. Also, purity improved as the heavy reflux fraction increased. The required target conditions for recovery and purity were achieved at a temperature of 150 °C and a heavy reflux fraction larger than 0.9 (Figure 3a). The simulation results (Figure 3) showed that the adsorbent Na-ETS-10 was able to achieve the purity and selectivity targets while other adsorbents like activated carbons were not. Na-ETS-10 had a significant C2/C1 selectivity which is a dominant requirement for the removal of C1 using a heavy reflux step.

4.4 Application 2 Hybrid GSP-PSA Process Design

4.4.1 Hybrid Optimized Model

As described in the May 2014 report [3], an Aspen Plus® simulation for the GSP and different GSP-PSA scenarios were developed to provide material and energy balance bases for the proposed adsorption cycle. In total, 24 different scenarios have been developed, simulated, and optimized for a GSP-PSA hybrid system.

The results of the optimization of 24 scenarios led to identification of the minimum acceptable PSA operating conditions for each scenario. This meant that recovery and purity of ethane in the C2 stream of the final PSA cycle design of U of A should have been more than these numbers for every given scenario. These constraints are presented in Table 1. The PSA cycle design by the U of A was adapted to the scenario of 2000 kPa column pressure (1% ethane content in the feed to the PSA), vacuum pressure of regeneration stage (10 kPa), compressor inside the PSA cycle, and PSA before the residue gas compressor (2400 kPa pressure feed to the PSA), as shown in Figure 2a. The minimum acceptable PSA performances were at least 50% ethane recovery from non-captured ethane in the residue gas of the base case and more than 70% purity. These have been achieved by the PSA cycle designed by the U of A (Figure 3a).

The final GSP-PSA hybrid configuration is shown in Figure 4. The resulting C1 stream from the PSA cycle is at a temperature of 150 ^{o}C. It is used to heat up the feed gas to the PSA by means of a heat exchanger. It is then recompressed up to 5000 kPa using the existing residue gas compressor and sent back to pipeline. The C2 stream, which is ethane rich (86% concentration), is cooled, compressed, cooled, chilled, and expanded before being sent to the demethanizer. The overall extra ethane recovery (ExRC2) using this combination was 84% of the current non-captured ethane (700,000 bbl/a). It should be noted that process integration, and in particular heat integration, between all existing and new streams was conducted.

4.4.2 GHG Impact Analysis and Economic Assessment

A GHG impact analysis and economic assessment for the final GSP-PSA process design was completed. Using an Aspen Plus® hybrid simulation, the extra power consumption by the PSA cycle (vacuum pump and compressor inside the cycle), residue gas recompressor, and C2 compressor (ExP (GWh/a)) was calculated.

GHG impact was also calculated as per the equation:

$$\text{GHG impact (ton/a)} = CO_2 \text{ equivalent of ExRC2} - CO_2 \text{ equivalent of ExP}$$

The "CO_2 equivalent of ExRC2" corresponds to the amount of CO_2 that would be generated if ExRC2 is burnt as fuel. Since the ExRC2 will not be burnt to generate CO_2, but instead will be converted to high-added value products such as ethylene, polyethylene, etc., the result is a positive impact in terms of GHG emissions. On the other hand, extra power for recompression is required to recover extra ethane. The "CO_2 equivalent of ExP" corresponds to the amount of CO_2 generation at power plants across the Province of Alberta. The major sources for electricity generation in Alberta are coal and natural gas, accounting for 52.5% and 37.5%, respectively [4]. This means that every MWh of electricity produced generates around 0.811 ton CO_2 [5].

Due to the fact that NOVA Chemicals does not own or operate any straddle plants (GSP), it is crucial that an economic analysis be completed in order to compare with other competing technologies. Multiple meetings have been held between the project team and the NOVA Chemicals ethane feedstock group to ensure the economic analysis aligns with the business needs. The extra capital and operating costs were estimated for hybrid system.

Table 2 summarizes the results of the GHG impact and economic analyses. The results showed that the hybridization process could recover 84% of current non-captured ethane from residue gas (700,000 bbl/a), however, the extra power consumption would be 420 GWh/a which is much larger than the current GSP process power consumption (168 GWh/a). This results in high energy intensity for extra ethane recovery compared to the current GSP (2172 vs. 116 MJ/bbl). In addition, it would lead to 27.3 M$/a of extra operating cost and increase GHG emissions by 225 ktonne/a. The capital cost to implement this project would be 72.0 M$. All of these resulted in a negative profitability index (PI = -1.7), which is very much lower than the baseline PI (= 1.0). Therefore, this project is neither economically viable, nor environmentally friendly.

4.5 Scorecard

As mentioned in the May 2014 report [3], based on the work at NOVA and the U of A, a scorecard has been prepared which contains criteria to decide whether to continue pursuing Application 2. This scorecard is shown in Table 3. All technical criteria, except the commercial availability of the adsorbent (non-commercial available Na-ETS-10 has been selected as the ideal adsorbent), led to a "Go" for this application. Nevertheless, the only environmental criterion

(GHG emission reduction) and two economic criteria (energy intensity and PI), have led to a "No Go" decision for this project.

4.6 Project Risk Register

A risk register was created to identify potential project risks [6]. No high level risks were identified. The following Medium level risks were identified:

i) C3+ feed components difficult to desorb

ii) Feed contaminants adsorbed

iii) Mechanical strength of ETS-10 inadequate

iv) Experimental errors lead to schedule impacts

5.0 Conclusion

Economic and environmental criteria show that this application is not an attractive technology for implementation. The reasons are primarily due to high energy intensity, negative environmental impact, high capital and operating cost, and finally, a negative profitability index. However, the PSA cycle design performs well in terms of high purity and recovery of ethane separation. The GSP-PSA hybrid process design showed a high extra ethane recovery of 84% from non-captured ethane.

6.0 Recommendation

As described in this report, NOVA Chemicals recommends to close-out this research activity. The separation of ethane/methane with a hybrid GSP-PSA system is not enabling due to high energy intensity, high capital and operating costs, and high GHG emissions.

7.0 Acknowledgements

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8.0 References

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9.0 Figures

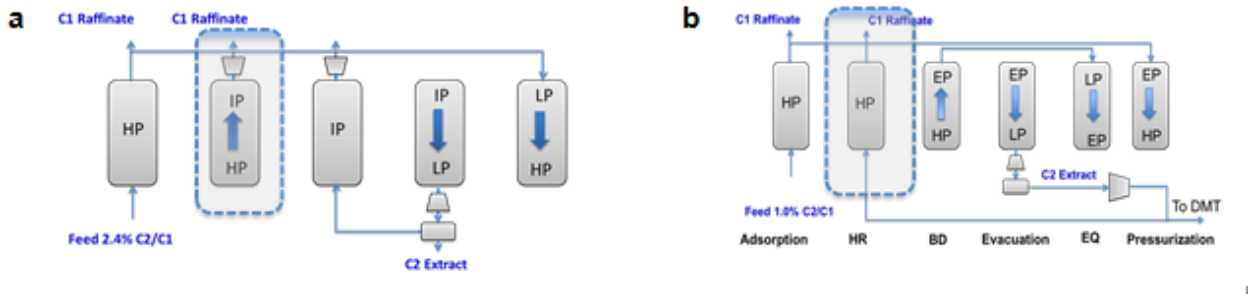

Figure 1 – (a) Schematic of the cycle developed in the Engage Grant, including light product pressurization (LPP) and heavy reflux (HR). b) Schematic of the cycle developed during the Engage Plus Grant, which includes a heavy reflux step at high pressure and pressure equalization (PE).

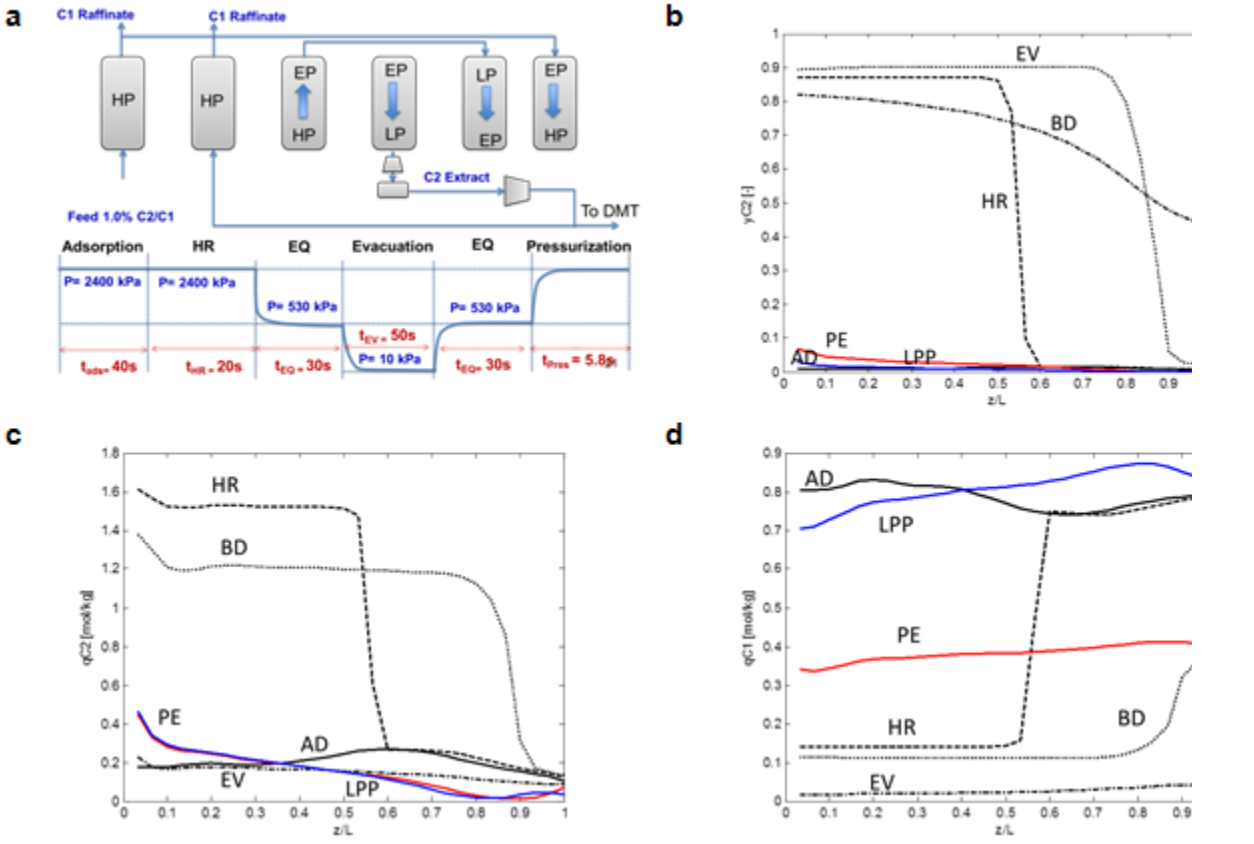

Figure 2 – (a) Schematic of the new adsorption cycle together with the corresponding pressures profiles for each step and the selected step times; (b) C2 gas phase compositions; (c) C2 adsorbate concentration; and (d) C1 adsorbate concentration along the bed length at the end of each step at cyclic steady state conditions. Feed temperature = 150 ºC, adsorbent material: Na-ETS-10.

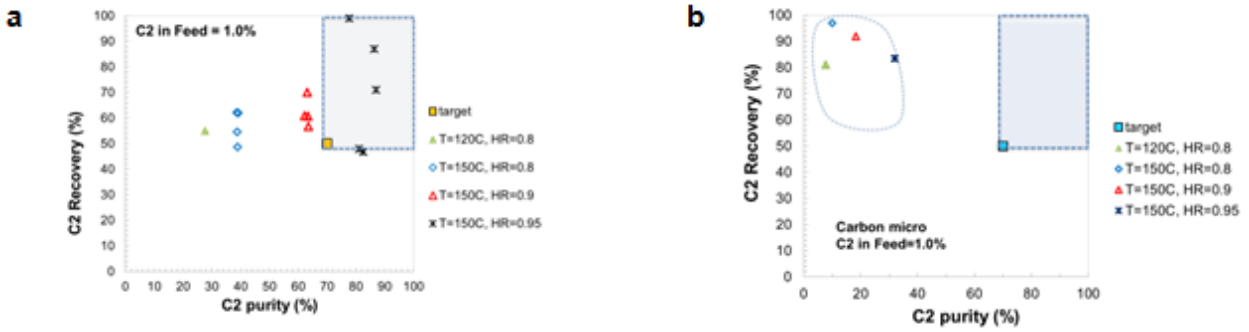

Figure 3 - C2 recovery vs. C2 purity. Adsorbent material: (a) Na-ETS-10 (different similar icons indicate different adsorption step length – higher recovery at shorter adsorption step of PSA cycle); (b) Carbon

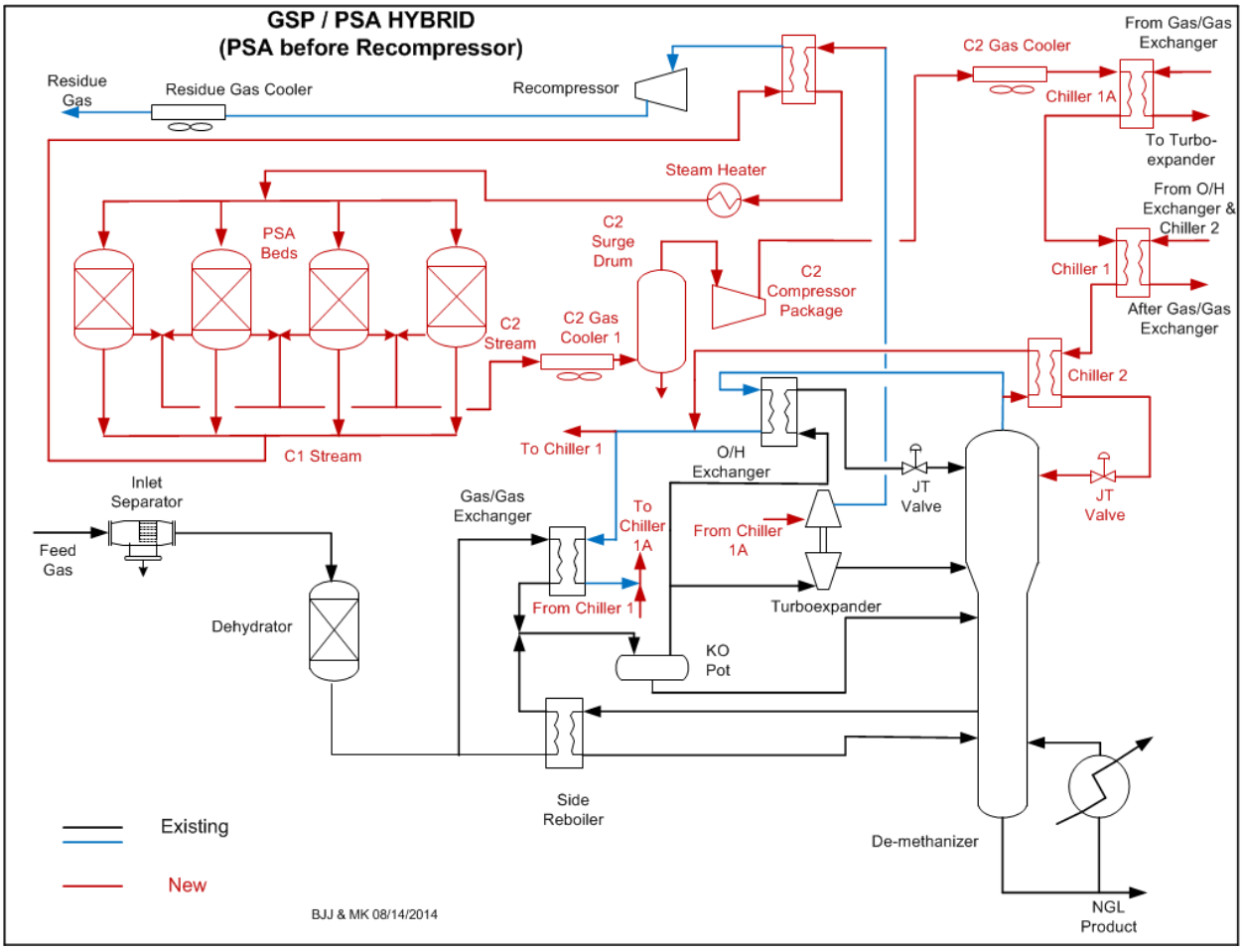

Figure 4 - The final GSP-PSA hybrid process design

10.0 Tables

Table 1 - Summary of minimum acceptable PSA performance

Column Pressure (kPa)	Pressure of Regeneration step of PSA (kPa)	Position of PSA in Hybrid System	Compressor inside PSA Cycle	Minimum PSA Purity (%)	Minimum PSA Recovery (%)
2000	10	Before Turboexpander compressor, before and after Residue Gas Compressor	With/out	70	50
	100			35	50
2300	10			85	80
	100			65	80

Table 2 - Summary of GHG and Economic Analyses Results

Parameter	Value	Note
Extra Recovered Ethane (bbl/a)	700,000	84% overall recovery of non-captured ethane using hybrid system
Extra Power Consumption (GWh/a)	420	vs. 168 in current GSP plant (energy intensity of 2172 vs. 116 MJ/bbl)
Capital Cost (M$)	72	PSA, compressor, HEXs
Operating Cost (M$/a)	27.3	Vacuum pump, compressor power consumption
Profitability Index (PI)	-1.7 < 1.0	Should be more than 1.0
Increase in GHG Emission (ktonne/a)	225	Does not reduce the GHG emission

Table 3 - Scorecard

Criteria	Go	Uncertain	No Go
420,000 bbl/a of extra ethane recovery (PSA recovery: > 50%)	x		
No additional residue gas compressor (C1 stream pressure drop from PSA: < 5 psi)	x		
C2 stream recycle to column: < 10% (PSA purity: > 9%)	x		
Acceptable PSA purity: > 70%	x		
Commercial availability of adsorbent			x
Energy intensity: < 165 MJ/bbl			x
Profitability index: > 1.0			x
GHG emission reduction			x