

New Energy Efficient Process to Capture CO₂ for CCS

Executive Summary

The *New Process* significantly reduces the life cycle cost (compared to other current state-of-the-art processes) for H₂S removal and Carbon Capture and Sequestration (CCS) from a synthesis gas following coal/coke gasification.

This new CO₂ capture process will achieve significant life cycle cost reduction compared to current technology. One of the features of the *New Process* is that it requires only equipment which is available in the market place today from multiple vendors, and does not require any new technology, such as new solvents, catalysts, or techniques.

The process contains elements of processes that have been commercially proven in separate applications. The uniqueness of the invention is in the combination and sequencing of the process elements and its integration through extensive heat recovery. The design of the *New Process* was a deliberate effort to ensure the process will be acceptable by funding sources such as banks, venture capitalists, and risk adverse companies to embrace the *New Process* to provide funding.

This summary is made within the context of extracting acid gas from synthetic gas generated by the gasifier in an IGCC project which includes full CO-Shift reaction and pre-combustion CCS. The objective is to capture the CO₂ cost effectively and to purify it so that it can be transported safely by pipeline in a supercritical state.

The two most generally employed processes used by industry to extract H₂S and capture CO₂ from a syngas stream are either Selexol™ or Rectisol®.

The Selexol™ process is based on a physical solvent, a blend of dimethyl ethers of polyethylene glycol (DEPG). This process operates at relatively warm temperatures and selectively extracts H₂S, but less optimally captures the CO₂.

The Rectisol® process is also based on a physical solvent, methanol, which operates at relatively colder temperatures than DEPG. The methanol solvent can more economically capture the high

concentration of CO₂ in the synthesis gas compared to DEPG, but unfortunately methanol is not as economical as DEPG at selectively absorbing H₂S in a stream containing both H₂S and CO₂ when both occur simultaneously.

Rather than applying only one of these technologies, either DEPG or methanol, to remove simultaneously the H₂S and capture the CO₂, the *New Process* utilizes the best attributes of each of these commercially available “open art” solvents sequentially as part of a 5-stage process.

Stages 1 and 2 are typical pre-conditioning processes, located upstream of the new pre-combustion carbon capture process. Alternative pre-conditioning processes are equally valid, providing that they deliver a high pressure synthesis gas to Stage 3 that is both dry and sulfur compound free (to comply with environmental permits). Besides DEPG, other examples of suitable preconditioning H₂S removal processes located upstream of the CO-Shift include NMP Solvent (Purisol Process), MDEA selective H₂S removal process, and potentially in the future, the Warm Gas Clean Up process under development with RTI.

Stage 1

H₂S is removed selectively from the synthetic gas leaving the gasification technical battery limits by a DEPG process (or other suitable H₂S selective removal process) prior to the CO-Shift reaction. The H₂S removed is sent to a Claus unit for further processing.

Stage 2

The synthesis gas is CO shifted and the resultant synthesis gas, comprising of mostly H₂ and CO₂, is then cooled and dewatered.

Stages 3 thru 5 are an integral part of the New Process, patent pending.

Stage 3

The high pressure, sulfur free, fully-dried synthesis gas is subjected to bulk CO₂ removal by way of condensation of the CO₂ by chilling the synthesis gas. The chilling is capable of removing about 30% to 80% or more of the CO₂ (depending on the partial pressure of the CO₂ in the synthesis gas stream). The higher the partial pressure of CO₂, the better for the new process as this will result in a

lower parasitic energy demand for recovering the CO₂, purifying it, and delivering it at supercritical pressure for export from the facility. The chilling is accomplished by application of progressively colder refrigeration, while being careful to avoid freezing the liquefied CO₂ at below minus 69 deg F in the final chiller.

Stage 4

Residual CO₂ in the synthetic gas (not extracted by the bulk CO₂ removal in Stage 3) is subsequently removed. This can be achieved by absorption into a refrigerated methanol stream which is then heated at pressure and then flashed within the range of 200 to 300 psia. The CO₂ flashed stream is compressed and cooled until it condenses. This CO₂ condensate is then added to the CO₂ stream extracted from the bulk removal Stage 3. (Variations of Stage 4, outlined in detail in the patent, allow for alternative methods of removing the residual amounts of CO₂. Such alternatives include use of different solvents, pressure swing adsorption (PSA), or the deliberate freezing of CO₂, and re-melting the solid CO₂ to a liquid).

Stage 5

The combined CO₂ liquid product stream is then purified by distillation.

This 5th Stage is carried out due to limitations in the granting of permits with 1,000 ppm CO specifications for new CO₂ discharge permits. Regulatory authorities increasingly have needed to tighten rules for permitting discharge streams of CO₂ to limit the CO specification at 200 ppm. This can occur when a municipality has already attained the maximum level of CO that can be discharged in their jurisdiction due to granting prior permits. This results in the late comer having to meet the more stringent CO specification.

This final stage in the *New Process* will reduce the CO content in the CO₂ to less than 200 ppm, along with recovering small amounts of hydrogen, nitrogen and methane by distillation purification. It is then possible to pump the purified CO₂ bottoms product to about 2,200 psia for custody transfer at the high pressure pipeline.

Overview

Information around the Selexol™ Process and the Rectisol® process are proprietary to UOP, Lurgi and Lindi respectively. The patents on these processes have long since expired, and the patent information is now in public domain and is freely available for use by the competitors of the original licensing firms.

Until relatively recently, the licensing firms had a tightly controlled monopoly on proprietary solubility and thermodynamic data. This made it impractical for competing engineering firms to provide alternative design options. Recent developments have shown that independent developers of Process Simulation software have been able to obtain real plant data. This plant data (for the Selexol™ and Rectisol® solvents) has been regressed in order to calibrate it, so as to fit the collected data into the process simulator. This has now opened up the possibility for engineering companies, using this independent simulation software, to provide a design to compete against the original patent holder.

Information provided in this document was derived by analysis of simulations carried out independently from any process licensor. Data for the equilibrium of solubility of acid gas constituents in the various solvents have not been extracted from any licensed proprietary information, only from the independent data results from plant simulation.

While there existed a monopoly of design data, held only by the licensor of each of the respective processes, each licensor would develop a process scheme that would best maximize their own competitive advantage. The situation has now changed and now there are new possibilities. One possibility is to “mix and match” the different strengths of each patented process. This has never been disclosed before, and it can only be accomplished now that solubility and thermodynamic data are freely available outside the original licensors’ control.

It is clear that the licensors have lost their tight grip on their design data. The licensors would not be pleased about this information spreading, since they will now be required to compete on an even playing field, as opposed to being the only company able to provide their specific technology.

The licensors will claim that the results are invalid, since the data used to generate the simulation results used in the independent software are not approved or provided by the licensor. But the software has been calibrated by real plant data, and on discussions with the plant superintendant of one facility, the software does an exceptional job of simulating the plant's operation. It is anticipated that there will be differences in the results generated by the independent software compared to the results provided by the licensors; nonetheless, there is sufficient confidence that the design uncertainty can be overcome by some modest design margin on the equipment specifications.

Background Information

Conventional wisdom has identified two competing processes following pressurized coal/coke gasification, needed for removal of sulfur species and for Carbon Capture and Storage (CCS). The two processes identified are the Selexol™ process, licensed by UOP, and the Rectisol® process, licensed either by Lurgi, or by Lindi. Both Lurgi and Lindi are European companies. Other possible processes have been identified, (including , Morphysorb, Purisol, and Propylene Carbonate for example), none of which have any commercial track record in processing synthesis gas derived from coal/coke gasification).

Further, in re-stating conventional wisdom, the Selexol™ two stage process has been identified as the process of choice to remove both sulfur compounds and to capture the CO₂ following a multi-bed sour CO-Shift reaction process. (It is also the one process used as the acid gas removal (AGR) process example presented in the DOE/NETL Report published in 2007, comparing the different major gasification technologies in power production, with and without CCS). The rationale, in comparing Selexol™ with Rectisol® is that the Selexol™ process is reputed to be less expensive and has a lower OPEX demand than Rectisol®. On the other hand, conventional wisdom states that the Rectisol® process is better at removing contaminants to a deeper level, including such compounds as H₂S, COS, and metal carbonyls. This fact would then make the Rectisol® process preferable in an application requiring high purity syngas such as in the manufacture of SNG, hydrogen, methanol, ammonia or Fischer –Tropsch products.

While some elements of the conventional wisdom stated above can be supported, there are some contradictions which prove to be exceptions to the rule. Experience will dictate when the exceptions are valid.

Relevant Insight for Process Selection between Selexol™ and Rectisol®

The exception to the general rule occurs when the design economy of scale requires that the project processes large volumes (say an IGCC with CCS power plant will require 3 or more operating gasifiers, processing about 8,000 or more tons of coal per day), then in this case, the Rectisol® process proves to be the more cost effective of the two processes, specifically for an IGCC with CCS having about a 90% or better capture rate.

Based on experience, a project using three E-Gas™ gasifiers (or other similar sized capacity gasifiers), with a large volume of gasification product synthesis gas to be treated, requires a minimum of 2 Rectisol® absorption towers and a common regeneration system; while the Selexol™ process requires a minimum of 3 full trains, consisting of 3 absorption towers as well as 3 complete regeneration systems.

The reason for this difference is partly due to the differences in the absorption temperature in the respective absorbers. The much colder temperature found in the Rectisol® process compared to the Selexol™ process reduces the raw synthesis gas flowing volume, which allows the “shrunk” volume to fit into the 2 Rectisol® absorption columns instead of the required 3 Selexol™ absorption columns operating at a warmer temperature. The solvent capacity of Rectisol® for absorption of carbon dioxide is much higher than the solvent capacity using Selexol™, requiring a single Rectisol® regeneration equipment train, while the Selexol™ process requires 3 regeneration trains to regenerate all the solvent used in absorbing the same quantity of carbon dioxide.

The fewer trains needed in the Rectisol® process compared to the Selexol™ process results in a significant CAPEX savings to the project due mostly to equipment piece count. The lower solvent circulation rate needed for Rectisol® results in a lower OPEX for Rectisol®, compared to Selexol™.

The significantly higher specific loading of CO₂ in Rectisol® process is released by flashing, leading to a sharp temperature drop of the solvent. The lowest process temperatures obtained this way are far below the level of Rectisol's refrigeration system and may, on occasion, reach down to – 95 deg F (though the coldest level on a typical IGCC with CCS application is around -75 deg F). The colder the solvent, the higher is the specific capacity for carbon dioxide. This leads to lower solvent circulation rates and an even sharper temperature drop of the flashing solvent. This is known as the auto refrigeration effect. The external refrigeration unit has to make up for heat gains which occur in the desulphurization and acid gas enrichment parts of the overall combined process. The refrigeration lowest temperature is about -45 deg F, allowing for a single refrigerant (propylene) to be used in a multi stage refrigeration compressor.

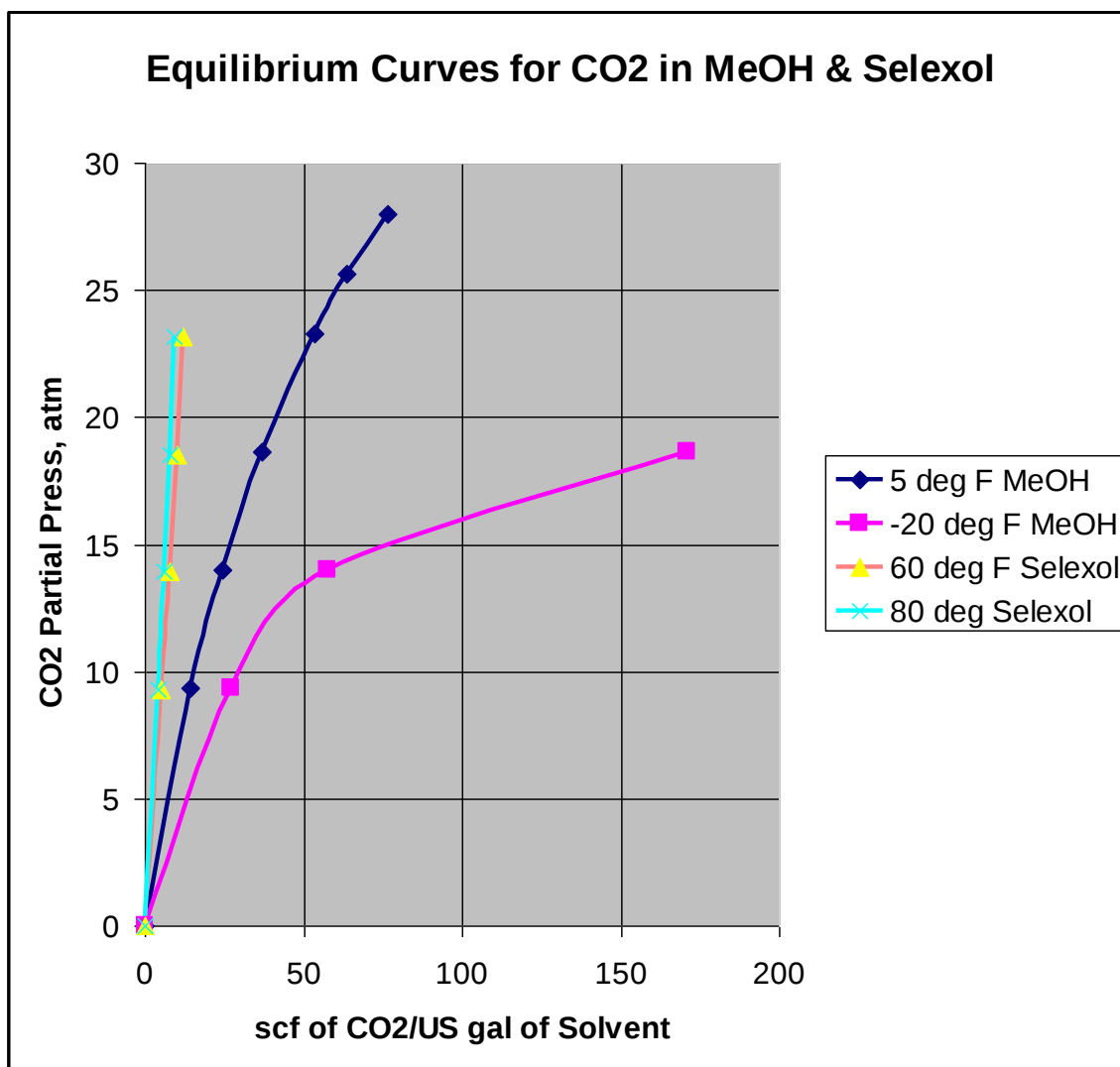
In contrast, while Selexol™ also benefits from the application of the colder solvent, the degree of coldness is limited to about +30 deg F. This limitation is due to the Selexol™ solvent's increasing viscosity in progressively colder temperatures, which limits its pumpability, absorption characteristics and heat transfer properties in heat exchangers. The auto refrigeration effect is thus limited, requiring significantly higher external refrigeration loads of Selexol™ process compared to Rectisol® to achieve the absorption of the same quantity of CO₂ at the same synthesis gas composition and conditions.

See the chart below - Equilibrium Curves for CO₂ in Methanol and Selexol™. This chart was developed using the ProMax simulation software. The typical temperature range at the bottom of the CO₂ absorption tower is bracketed. For Rectisol®, the typical temperature range is from +5 deg F to -20 deg F. This temperature is the warmest part of the absorption tower, since the CO₂ on absorption, causes the liquid solvent temperature to rise (due to the heat of absorption). The coldest part of the system occurs after the CO₂ is flashed at the lowest pressure, allowing the heat of CO₂ desorption to cool the solvent temperature to low levels as described above. The typical temperatures encountered in the bottom of a Selexol™ CO₂ absorption column is around 80 to 60 deg F. This limits the coldest temperature being formed on the flashed solvent at around +30 deg F.

The colder temperature curves (in both processes) are favored by the higher CO₂ partial pressure gas streams to be treated. A fully shifted gas would result in the colder temperature, while partial

shift will remain between the bracketed temperature, and non shifted syngas will result in the warmer end of the range.

Selexol™ has a significant advantage when selectivity of H₂S over CO₂ is the goal. This feature makes Selexol™ a good choice whenever there is no carbon capture needed, such as IGCC applications without carbon capture. The selectivity of H₂S over CO₂ results in the low capacity for CO₂ and therefore relatively very high Selexol™ solvent circulation rates on the CO₂ removal section of the overall 2-stage Selexol™ AGR process.



Guidelines for Project Selection Between Using Selexol™ or Rectisol® Processes

One needs to be cautious of claims that “since the Selexol™ solvent operates at a warmer temperature than Rectisol® it stands to reason that the power for refrigeration is less in the Selexol™ process compared to Rectisol® process”. This is only true if there is little or no CO₂ capture required. Whenever modest and especially substantial amounts of CO₂ are to be captured, (such as in a fully CO-Shifted synthesis gas), then the refrigeration loads for the Rectisol® process are significantly lower than for the Selexol™ process.

The Rectisol® process has no limitation to how cold the methanol can reach, so it can take complete advantage of the auto-cooling effect described. Whereas, the Selexol™ process would encounter operating difficulties whenever the auto-cooling effect results in temperatures below the critical threshold, thereby requiring the design to limit the auto-cooling effect to less than 100% of what is available. The balance of cooling will require external refrigeration to make up for the loss of the full auto-cooling effect.

In summary, with high pressure applications, (450 psig or higher) whenever carbon dioxide removal is part of the project requirements (such as in SNG, Fischer Tropsch, hydrogen, ammonia and methanol manufacture as well as IGCC - with carbon capture), then the Rectisol® process is the leading candidate process. Whenever there is no requirement for capturing carbon dioxide such as IGCC without carbon capture and NG applications with little CO₂ removal required, then Selexol™ is the more appropriate process.

With smaller projects, in which only one AGR train (Selexol™ or Rectisol®) is applicable, then there may require a CAPEX versus OPEX life cycle analysis to determine the most cost effective process. In this case the OPEX favors Rectisol® and CAPEX may favor Selexol™. In larger AGR projects, in which multiple Selexol™ trains are required to process the volume of raw gas, the CAPEX and economy of scale favors the Rectisol® process over Selexol™. The Rectisol® OPEX always favors Rectisol® if H₂S is removed and large amounts of CO₂ are also needing to be captured, (for example, in a project with IGCC followed by CCS in which 90% CO₂ is captured).

Stepping Outside the Box

See the following table - Physical Solvent Solubility Data. The table is helpful in understanding the capabilities of the potential solvents under consideration. The physical absorption of acid gas constituents are required from a high pressure synthesis gas stream, high in CO₂ concentration, following the CO-Shift reaction in multiple CO-Shift beds (typically 2 or 3 beds).

DEPG, is the non-proprietary name used for the solvent used in the Selexol™ process, it is a blend of Dimethyl Ethers of Polyethylene Glycol, - DEPG for short. DEPG has a formula CH₃O(C₂H₄O)_nCH₃. On reading the original Allied Chemicals patent, n is stated to lie in a range between 3 and 9.

This table is based on the solubility of the acid gas constituent (by itself) at atmospheric partial pressure. Below the table, the ratio of solubility of H₂S relative to CO₂ can be seen. This is the measure of the selectivity of the solvent for H₂S in preference over CO₂. The most interesting entries fall under DEPG or NMP since they provide the largest selectivity for H₂S. The next most interesting entry is the solubility of CO₂ (on an H₂S free base) for methanol at – 25 C (-13 F). The CO₂ solubility is about 3 ½ times greater in methanol than in DEPG at 25 C).

The selectivity for H₂S over CO₂ in methanol improves with colder temperature. At about -75 F, the relative selectivity is about 6:1. So at the top of the Absorber Rectisol® column, where the coldest methanol is introduced, the selectivity for H₂S over CO₂ is as much as 6:1. However, due to the heat of absorption, by the time the solvent has picked up the CO₂ and is approaching equilibrium at the bottom of the absorber, the methanol is at roughly -25 C, (13 F), where the selectivity of H₂S over CO₂ has declined to less than 5.

The table helps to explain why the Rectisol® process requires more equipment (a higher CAPEX) to selectively separate H₂S from CO₂ compared to the DEPG process. The lower selectivity of H₂S in methanol at the bottom of the absorber tower conditions compared to DEPG at the bottom of its absorption tower requires that the methanol solvent will need to first flash the absorbed acid gas, and then to re-absorb the acid gas at lower pressure, (this is acid gas enrichment) and this is needed in order to improve the relative concentration of H₂S over CO₂, so

that the acid gas stream can be cost effectively treated in a Claus or Oxy-Claus plant. But in the case of DEPG, it has twice the selectivity of H₂S over CO₂ at the temperature conditions at the bottom of the Absorber tower, and is therefore capable of selectively concentrating the H₂S in a single absorption step, making the DEPG the better solvent for selectively removing H₂S, compared to methanol.

Physical Solvent Solubility Data

Solubility Data (Nm³ Gas/m³ Liquid)

	DEPG	NMP	PC	Methanol
Component	(Selexol)	(Purisol)	(Fluor Solv)	(Generic)
Temp	25 C	25 C	25 C	-25 C
CO ₂	3.69	3.42	3.53	13.24
H ₂	0.02	0.02	0.03	0.07
CO	0.06	0.07	0.08	0.14
CH ₄	0.23	0.25	0.29	0.73
COS	12.20	10.19	15.10	56.76
H ₂ S	37.00	30.94	14.51	64.90

DEPG Dimethyl Ethers of
Polyethylene Glycol

NMP N-Methyl-2-Pyrrolidone

PC Propylene
Carbonate

Selectivity

H ₂ S:CO ₂	10.03	9.05	4.11	4.90
COS:CO ₂	3.31	2.98	4.28	4.29

London Management, Inc.¹

New possibilities arise, once one is empowered to disregard a licensor's requirement that his single solvent must be used to accomplish both selective H₂S removal and CO₂ capture.

A study of the above table, along with other considerations, will lead to the following conclusions:

- H_2S is to be removed first, selectively, by DEPG.
- The selective removal of H_2S is to be carried out prior to CO Shift conversion. This will provide the easiest (least expensive design for a DEPG plant since the relative concentration of H_2S : CO_2 in the feed gas to be treated is greater prior to CO-shift compared to post CO-Shift. Also, this will provide the least costly design of an Oxy-Claus Plant, because the DEPG plant design will produce a higher relative H_2S concentration in stripper overhead gas feed to the Oxy-Claus Plant, compared to removing the H_2S selectively downstream of the CO-Shift reaction.
- Bulk removal of CO_2 from a sulfur and moisture free stream can be most cost effectively carried out via condensing the CO_2 at high pressure. To accomplish this, it is important to stay a degree or two warmer than the freezing temperature of CO_2 (-69 deg F), while also maintaining the pressure of the gas stream at as high a pressure as available from the feed gas. The bulk condensation step could remove economically between 30 % to 70 % or more of the CO_2 . The degree of CO_2 condensed in this way is dependent on the partial pressure of CO_2 in the feed gas. The higher the feed gas pressure and the higher the CO_2 concentration in the feed gas, the higher is the partial pressure of CO_2 , leading to more bulk recovery of CO_2 at this condensation stage.
- Residual CO_2 (not condensed in the bulk CO_2 removal condensation step) remains in the vapor state. The CO_2 removed from this residual vapor is to be removed by a separate refrigerated methanol solvent downstream from the CO Shift section, since methanol's solvent capacity to hold CO_2 is several times greater than DEPG, and requires less external refrigeration energy. Furthermore, the coldest flash temperature is not limited in the case of the methanol solvent, whereas the coldest temperature is limited with the DEPG solvent - which increases the DEPG viscosity excessively, when it is cooler than 0 deg C. Since the methanol will be required to capture CO_2 in the absence of H_2S , there is no need for expensive equipment to enrich the H_2S , (since there is no H_2S to enrich).

- The CO₂ captured in the refrigerated methanol solvent is then heated and released at as high a release pressure as possible. This will save one or two compression stages of the CO₂ re-compressor needed to raise the pressure of the residual CO₂ (not already removed in the bulk condensation step) to a pressure level suitable for condensing the vapor CO₂ at a convenient level of available refrigeration. The work carried out to date has shown that a heated methanol stream can be regenerated in the range of 200 to 300 psia. The higher the pressure the better in order to minimize CO₂ recompression costs. The trade off is that as the pressure is raised toward the upper level of the pressure range, there is an amount of methanol which will stay in the vapor phase along with the released CO₂. This vaporized methanol will need to be removed from the released CO₂, by further cooling and condensing the methanol, while leaving the CO₂ still in the vapor phase (or by using a molecular sieve – or some combination). Upon removal of the methanol from the CO₂, the next step is to condense the CO₂ at the selected pressure in the range of 200 to 300 psia, and then to combine the liquid condensate CO₂ just formed, with the CO₂ already collected via the bulk CO₂ removal step, using the initial condensation step.

These observations address the foremost issues of H₂S removal and CO₂ capture for storage. One other serious issue, not addressed thus far, is the impact of residual CO left in the CO₂ stream intended for geological storage.

The Problem of CO in the Stream intended for Storage

One problem shared by physical absorption processes (both DEPG and methanol), is the small amount of CO co-absorbed by the physical solvent. This co-absorbed CO will end up in the regenerated CO₂ stream. Injecting the small amount of CO along with the captured CO₂ into the geological storage formation is not a problem. The problem occurs in the case of an accident. Environmentally high levels of CO in the CO₂ (over 1000 ppm) could potentially be accidentally emitted with the CO₂ stream in the event of equipment failure. One potential source of CO₂ discharge is through a pipeline breakage, leading to CO₂ emissions. Another failure, (not so catastrophic), is mechanical compression or injection equipment failure requiring a stoppage of the CO₂ flow from the carbon capture process. With no place to send the captured CO₂, the power plant would likely have to temporarily emergency discharge the CO₂ to atmosphere, until

the compression/pipeline /injection equipment can be fixed, or while the power plant is placed under controlled shut down, or placed on hot stand-by. With high contaminant levels of CO in the CO₂, this would be prohibited by the environmental air permit, and an immediate emergency shutdown would be required.

It should also be noted that some permitting authorities will not give a permit for a CO₂ discharge stream with over 200 ppm CO, this was the case in two of the authors experience on projects where the area CO limit had already been attained, and there was no possibility of permitting a new source CO₂ stream with a 1000 ppm CO specification. This was because specific permitting authorities had a tighter emission limit, due to existing permits already issued.

One solution to the low CO specification limit on product CO₂ is to revise the DEPG regeneration scheme to meet a CO₂ 200 ppm CO specification. This could be achieved by increasing the number of flash stages, and adding additional flash re-compressors. In this typical 2-stage DEPG configuration, it was required to use additional stages of flash, where both a first stage and a second stage flash gas steam would each be recompressed to the absorber pressure, and the remaining stages of flash released the CO₂ at several pressures, ranging from over 50 psia to about 7 psia (sub atmospheric). The various discharge CO₂ flash streams were then, most economically, compressed in stages to battery limits to substantially above the CO₂ supercritical pressure to about 2200 psia. (This additional equipment requirement significantly added both CAPEX and OPEX to the standard 2-stage DEPG configuration normally used to process a CO limit of 1000 ppm in the product CO₂ stream).

One other solution to the equipment failure scenario is to install a standby oxidizer device. In an emergency, the oxidizer (maintained in a hot standby condition) would catalytically oxidize the CO with added O₂ in the CO₂ vent stream at atmospheric pressure. One (or more) of the flash CO₂ streams is mixed with pure oxygen and fuel to achieve an incineration temperature needed to remove the entire residual CO by oxidation reaction. The lower pressure flash stream(s) may be able to bypass the incinerator if its CO levels in that CO₂ stream are within the permitted specifications. While this approach is technically feasible, the CAPEX and OPEX are

exceedingly high, and it is particularly galling to invest in the standby equipment that is not expected to be used).

These approaches are described in the paper presented at the IChemE, Amsterdam, 5th October 2010

Title: “Design and Operational Strategies for IGCC with Capture”, Authors: George Booras, Chris Higman, Dan Kubek, Jim Sorensen, Doug Todd. Paper is presented on behalf of the Electric Power Research Institute -- Palo Alto, CA & Charlotte, NC, USA.

A completely different approach is to remove the CO from the captured CO₂ by first liquefying the CO₂, then purifying it by distillation. This approach is economically feasible with the New Process (patent pending), but this approach would suffer a severe penalty if it was applied to the conventional DEPG 2-stage process or the conventional methanol absorption processes, in which the fully captured streams are discharged by flash at 2 or 3 stages, at close to atmospheric pressure.

Major Benefits of the New Process (Patent Pending)

The major benefits of the New Process (patent pending) over the current state-of-the-art process for CCS following IGCC are:

- 1) Lower energy required
- 2) Lower CO specification in the product.

New Process (Patent Pending) – Comparative Results

The following table is the results of several comparisons made for the energy consumed in removing H₂S selectively from a synthesis gas and capturing over 90% of the CO₂ following an E-Gas™ gasifier with full CO-Shift, while processing the product CO₂ to a level of CO concentration of less than 200 ppm.

Results Comparison Table DEPG AGR vs. New Process (Patent Pending)						
Plant A	CO Limit in CO ₂ Captured Stream	=	1,000	ppm		
	Power for DEPG AGR Plant	=	28,077	kW		
	Power For CO ₂ Compression (84% polytropic effcy)	=	44,000	kW		
	Total Power	=	72,077	kW		
	Total CO ₂ Recovered (at high pressure)	=	26,307	lbmole/hr		
	Power Required per lbmole of CO ₂ Captured	=	2.740	kW/Captured CO ₂ lbmole		
Plant B	CO Limit in CO ₂ Captured Stream	=	200	ppm		
	Power for DEPG AGR Plant	=	27,537	kW		
	Power For CO ₂ Compression (84% polytropic effcy)	=	20,899	kW		
	Total Power	=	48,436	kW		
	Total CO ₂ Recovered (at high pressure)	=	11,275	lbmole/hr		
	Power Required per lbmole of CO ₂ Captured	=	4.296	kW/Captured CO ₂ lbmole		
New Process - Cryogenic Separation + Methanol Absorption	CO Limit in CO ₂ Captured Stream	=	113.6	PPM		
	Total Power	=	82,687	kW	See Note 1	
	Total CO ₂ Recovered (at high pressure)	=	59,850	lbmole/hr		
	Power Required per lbmole of CO ₂ Captured	=	1.382	kW/Captured CO ₂ lbmole		
New Process - Cryogenic Separation + Adsorption Without Recycle	CO Limit in CO ₂ Captured Stream	=	10	PPM		
	Total Power	=	91,010	kW	See Note 1	
	Total CO ₂ Recovered (at high pressure)	=	58,515	lbmole/hr		
	Power Required per lbmole of CO ₂ Captured	=	1.555	kW/Captured CO ₂ lbmole		
New Process - Cryogenic Separation + CO ₂ Freezing and Melting	CO Limit in CO ₂ Captured Stream	=	228	PPM		
	Total Power	=	125,266	kW	See Note 1	
	Total CO ₂ Recovered (at high pressure)	=	61,239	lbmole/hr		
	Power Required per lbmole of CO ₂ Captured	=	2.046	kW/Captured CO ₂ lbmole		
Note 1: Includes the refrigeration loads within DEPG - H ₂ S removal and the mol sieves plants						

This is an apples-to-apples comparison, encompassing all the electrical loads in the H₂S selective removal plant, the CO₂ capture plant and the CO₂ compression plant in each case.

The DEPG process energy requirements are based on the appropriate configuration necessary to limit the CO in the discharged CO₂ stream prior to compression.

The 3 last processes in the above table are described in some detail in the new process licensor's website: (see www.ArnoldKeller.com Patent Application). The results are based on the detailed simulation of the New Processes, patent pending. No attempt was made to improve the CO concentration in the CO₂ from the last simulation results, since there were already 2 other variations of the New Process which showed a better result. This aspect of the last simulated results could be revisited later, if there is a good reason to do so.

The energy benefit of the New Process (patent pending) over the conventional DEPG 2-stage process, depends on the required CO₂ specification for limited CO concentration. Reviewing the

above table, it will be noted that: at the higher limit level of 1000 ppm CO allowed in the CO₂ stream, the calculated power benefit (basis kW/lbmol of CO₂ captured) is 1.445/2.74 or 47% less power. While for the lower 200 ppm level of CO in the CO₂ stream, the benefit is 1.445/4.269 (kW/lbmol of CO₂ captured) or 66 % less power.

The Following is a Summary of the Invention, Extracted from the Patent Application

[001] *Another embodiment of the present invention concerns a method of recovering carbon dioxide (CO₂) in a liquid state from a high-pressure gas stream. The method comprises cooling and partially condensing a high-pressure feed gas stream to thereby provide a condensed CO₂-rich fraction and an uncondensed CO₂-lean fraction. The method comprises recovering a CO₂-rich liquid stream from at least a portion of the uncondensed CO₂-lean fraction, wherein the recovering comprises one or more of the following steps: (1) absorbing CO₂ from the uncondensed CO₂-lean fraction, and/or (2) adsorbing CO₂ from the uncondensed CO₂-lean fraction, and/or (3) freezing CO₂ from the uncondensed CO₂-lean fraction. The method comprises introducing at least a portion of the CO₂-rich liquid stream recovered in step (b) and/or at least a portion of the condensed CO₂-rich fraction resulting from the cooling and partially condensing of step (a) into a purification zone and separating at least a portion of the non-CO₂ components from the CO₂-rich liquid stream and/or the condensed CO₂-rich fraction introduced into the purification zone to thereby provide a purified CO₂-rich liquid stream. Each of the high-pressure feed gas stream, the condensed CO₂-rich fraction, and the purified CO₂-rich liquid stream has a pressure greater than 77 psia.*

[002] *Carbon dioxide recovery processes and systems configured according to one or more embodiments of the present invention can comprise a first separation zone, for removing CO₂ from a substantially dry and nearly sulfur compound-free high pressure feed gas stream and a second separation zone for further separating CO₂ from the remaining feed gas stream by adsorbing, absorbing, or solidifying by freezing at least a portion of the CO₂ remaining in the feed gas stream. The processes and systems of the present invention can be more efficient, and thereby provide a bigger economic advantage, than conventional CO₂ capture and removal systems and processes. Processes and systems as described herein can minimize energy consumption by maintaining the pressure of one or more of the feed gas stream, the recovered, purified CO₂ liquid stream, and/or one or more interim process streams (e.g., the condensed CO₂-rich fraction withdrawn from the first separation zone and the CO₂-rich liquid stream exiting*

the second separation zone) at a pressure greater than 77, 100, 500, or 650 psia. In another embodiment, the pressure of one or more of these streams can be at a pressure greater than the triple point pressure of CO₂ (e.g., 77 psia), and/or at a pressure in the range of 77 to 1070 psia, 640 to 1016 psia, or 700 to 910 psia.

Impact on the New Process (patent pending) when varying the methanol circulation rate

The New Process, (with the methanol option used in the 2nd separation zone) is the case described in the “Results Comparison Table DEPG AGR Vs. New Process (Patent Pending)” See above. This is the base case for a further evaluation study. In this study, the investigation set out to determine the impact of both increasing and reducing the methanol circulation rate from the base case. As expected, this resulted in more or less CO₂ captured, compared to the base case. The energy consumed will also vary accordingly. The table below shows the results of the same simulation where the only changes made were the methanol circulation rate. The power consumed compared to the percentage CO₂ captured is an almost linear relationship in the range explored.

	Methanol Circulation	Factor	Power Consumed	% CO2 Recovered	CO Spec in CO2	CO2 Captured	Benchmark Plant A
	lbmol/h		MW	%	ppm	kW/lbmol CO2	Per Cent Savings
	49,875	0.70	74.313	87.60	87.6	1.322	48.25% 51.75%
	57,000	0.80	77.141	91.30	100.4	1.343	49.01% 50.99%
	64,125	0.90	79.926	93.21	108.7	1.363	49.74% 50.26%
BASE	71,250	1.00	82.687	95.15	113.6	1.382	50.44% 49.56%
	78,375	1.10	85.335	96.93	115.4	1.400	51.09% 48.91%
	81,740	1.15	86.478	97.51	115.4	1.410	51.46% 48.54%

Modification of an Existing IGCC Plant without CCS to become CCS Compliant

When an existing IGCC plant that uses Selexol™ as the H₂S selective process needs to be modified to incorporate carbon capture sequestration (CCS), there are several ways to go about it. Based on this discussion, one of the better options is to use an independent methanol solvent for capturing the CO₂. However, an even better economic option is to use the New Process (patent pending). This New Process is the perfect fit for modifying an existing IGCC plant without CCS and making it compliant for CCS.

Application of the New Process (Patent Pending) for NG Power Plant

The author plans to perform a new study, to evaluate the benefits of power production using the New Process (patent pending) when the feed gas is not coal derived synthesis gas, but natural gas (NG) instead. This study has become topical since there has been an increase in the amount of NG available in the USA and in other countries, since the development of new techniques for extracting NG from tight shale rock formations. These techniques are becoming more prevalent and are commonly referred to as “Hydraulic Fracking.” The description of the new technique is outside the scope of this report, but the evidence points to a stabilization of NG prices in the USA over the last 5 years (in spite of highly volatile oil price spikes), in most part due to the increase in NG supply as a result of Fracking. Going forward, it is possible that new power plant owners may choose to use a much less capital intensive power plant with CCS using NG instead of coal as the fuel of choice. The economic drivers are still in flux as various teams work through the coal versus NG competitive alternatives, and there continues to remain uncertainty on the potential of Federal environmental regulations limiting CO₂ emissions.

The application of the New Process is expected to be relevant if the NG was first converted to hydrogen, and the CO₂ was captured at pressure using the New Process briefly outlined above. The economics of carrying out this process will require there to be an environmental penalty for discharging CO₂ in the atmosphere. The penalty cost and or the selling price of CO₂ for industrial applications (such as EOR for example) would be a prerequisite to make such a scheme economically viable. Without a penalty price for emitting CO₂, or without the incentive to capture and sell the CO₂ at a profit, there will be no incentive to capture CO₂ for sequestration. If NG were to be the fuel of choice for new power plants, and there is an economic incentive to capture the CO₂, then there are several post combustion processes available to compete against the proposed New Process using pre-combustion. Eventually it will become clear which concept, and which process will prevail.