

COMPARING SELECTED POST- AND PRE-COMBUSTION ROUTES TO CO₂ CAPTURE: TECHNICAL & ECONOMIC CONSIDERATIONS

Presented at:
The Catalyst Group Resources™

Contact Details: John J. Murphy
Phone +1 (215) 628-4447
Email: John.J.Murphy@catalystgrp.com

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By: Arnold Keller, Process Engineering Consultant
London Management, Inc., Las Vegas, Nevada
www.ArnoldKeller.com

Introduction

For this brief presentation, the goal is to select a couple of the processes that were documented at length in the TCGR post combustion topics of the CC program, as well as a couple of the processes from the pre-combustion CC topics. The detailed reports are a matter of record and can be reviewed again at your convenience.

The objective of the presentation is to compare the most “imminent” contenders for CC for both the post-combustion and the pre-combustion alternatives on a side-by-side basis.

The analysis provided in the detailed report, as well as this presentation is exclusively developed from information available in the public domain.

Agenda

- Starting Point: DOE/NETL Comparative Study
- Post-Combustion Carbon Capture
 - MHI KM CDR (Sterically Hindered Amine)
 - Alstom CAP (Chilled Ammonia Process)
- Pre-Combustion Carbon Capture
 - Selexol™ (DEPG) and Rectisol® (Methanol)
 - New Integrated Process (Patent Pending)
- Comparative Summary

The starting point for the presentation is a DOE/NETL study published in 2007. In this report, there were 12 cases analyzed. The study compared IGCC with and without pre-combustion CC for three gasification technologies -- GE, E-Gas and Shell.

Other cases looked at pulverized coal combustion using sub-critical and super-critical steam boiler technology with and without post combustion CC.

Yet other cases compared using NG in a combined cycle, with and without post combustion CC.

For the post combustion PC technology CC, the technology selected in the DOE report was a MEA based amine (first generation process) commercialized by Fluor in their Econamine FG post combustion CC process.

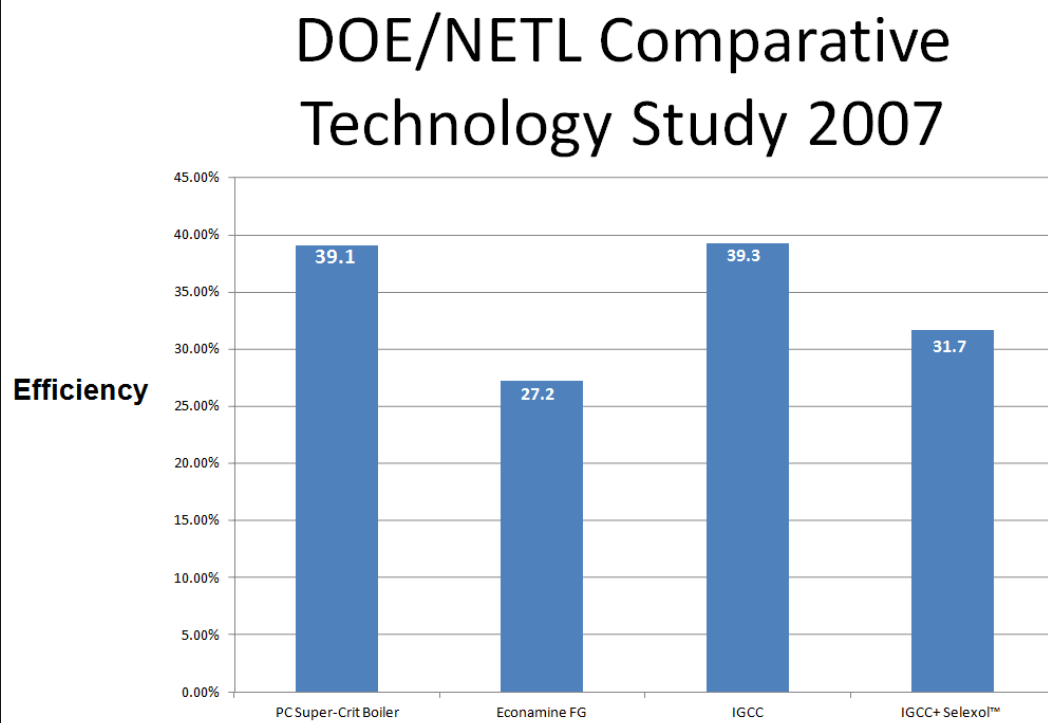
The detailed report issued for the first TCGR consortium study last year included 2 second generation processes. The first was developed by Kansai and Mitsubishi Heavy Industries (MHI), the KM CDR process – The “Kansai Mitsubishi Carbon Dioxide Recovery” (KM CDR) process. The second of these detailed processes was Alstom’s Chilled Ammonia Process (CAP).

The second report issued for TCGR Consortium this year focused on pre-combustion CC processes. The two state-of-the art processes are Selexol™ and Rectisol®. The Selexol process is licensed by Honeywell’s UOP division (and alternatively provided by The DOW Chemical Company). The generic version of the same solvent is available from Costal Chemicals. The solvent from Costal Chemicals is provided without any process guarantees and is used at the owners’ risk.

The Rectisol process is licensed by both Linde (a German company), and by Lurgi, (recently purchased by Air Liquide, a French company). The solvent used in the Rectisol process is Methanol -- a relatively inexpensive commodity chemical.

The final example of pre-combustion CC is a brand new process which was developed to reduce energy costs and to capitalize on combining proven, commercialized, current processes in a new integrated method, which enables substantial electric power savings over the current state-of-the-art process.

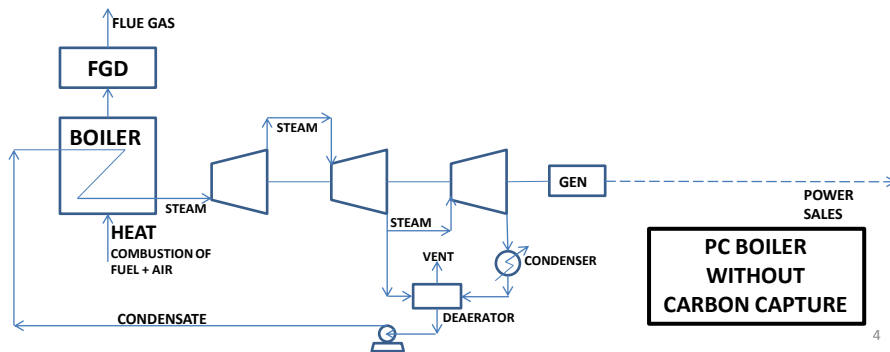
In the end, all the processes are compared side-by-side on an overall efficiency basis.



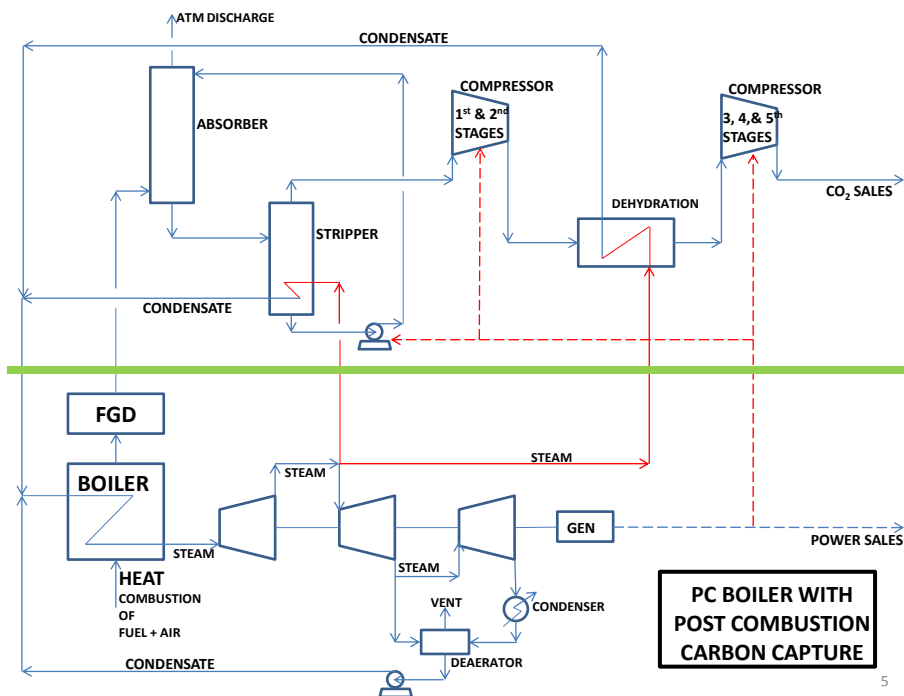
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For this presentation, 4 of the 12 DOE/NETL studies are compared based on efficiency.

You will notice the similar result of super-critical PC technology is almost identical to IGCC without CC. However, after requiring CC at 90% of the CO₂ discharged, the result shows a smaller power penalty for the IGCC case, compared to the super-critical PC technology.



Slide 4 shows a simplified block diagram for the a PC technology without CC



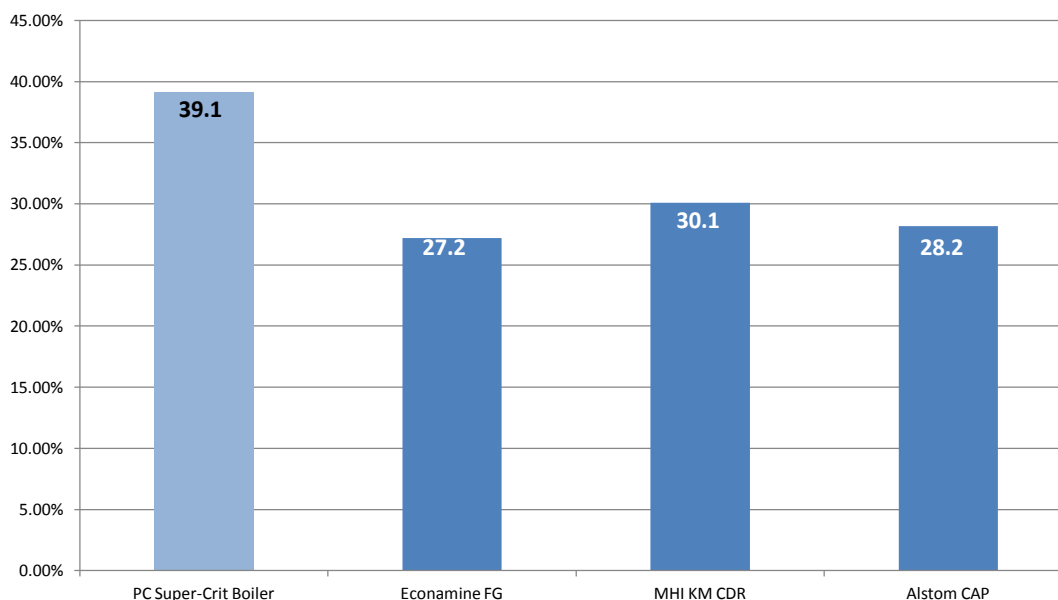
Slide 5 shows the added equipment required when you want (or are obliged) to “go green.” The additional equipment is needed to capture CO₂ post combustion.

The exhaust flue gas is desulfurized to a low level, and is then contacted by a lean solvent to absorb the CO₂. The rich solvent is regenerated in a steam heated stripper arrangement, releasing a water saturated CO₂ stream at atmospheric pressure. This wet CO₂ stream is then compressed, dried and additional compression is needed to reach the CO₂ discharge super-critical pressure for pipeline transmission.

The different technologies use different solvents. The lower the energy needed for regeneration of the solvent, leaves more steam to make more power. If the solvent releases the CO₂ at atmospheric pressure, then all the CO₂ will be compressed to super-critical pressure in 5 stages, with drying occurring typically after the 2nd stage of compression.

The red lines show where the parasitic power is consumed by the post combustion CC process. Most of the parasitic power is lost in the steam regeneration. A substantial loss occurs in the compression of CO₂ to supercritical pressure.

Overall Impact of Efficiency of CC on PC Fired Power Production with different Technologies



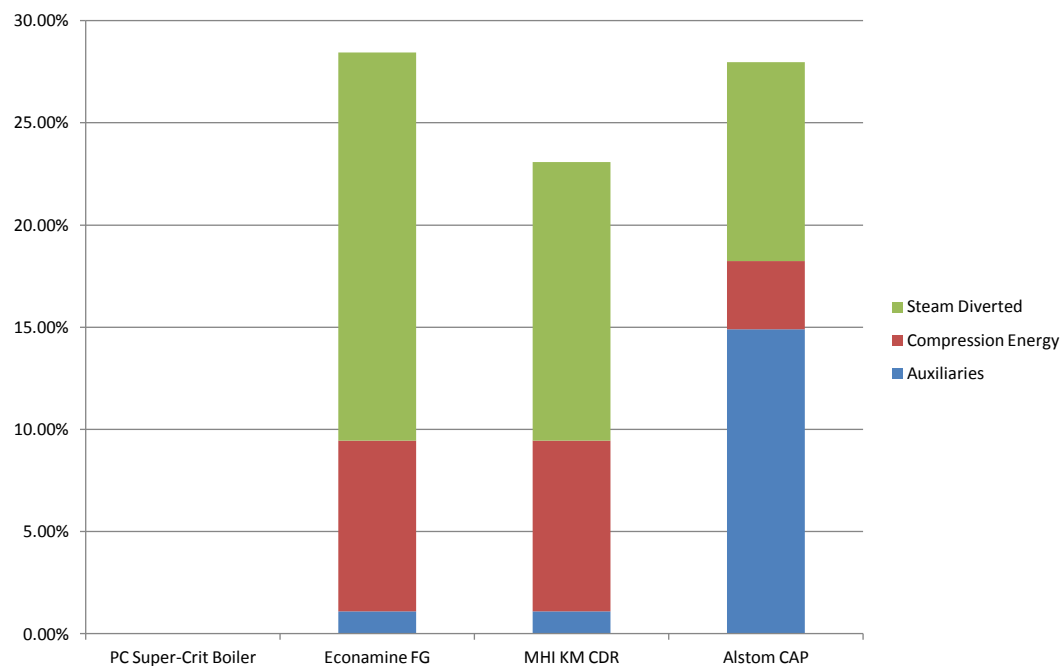
Slide 6 shows the net effect of post combustion CC on a PC supercritical technology, using the different solvents. Solvents with the least requirement of regeneration heat are most advantageous.

The least amount of heat needed to regenerate the CO₂ is from the Alstom CAP process. It is lower than both Econamine FG, and the KM CDR process, so the first inclination is to assume the Alstom's CAP process would prove to be the best.

Furthermore, Alstom's CAP process is designed to discharge its CO₂ at a pressure of roughly 300 psig (saving about 2 stages of compression).

Something else must be going on in the CAP process for it to be less effective than the KM CDR process. What could it be?

Post-Combustion CC Parasitic loss breakdown



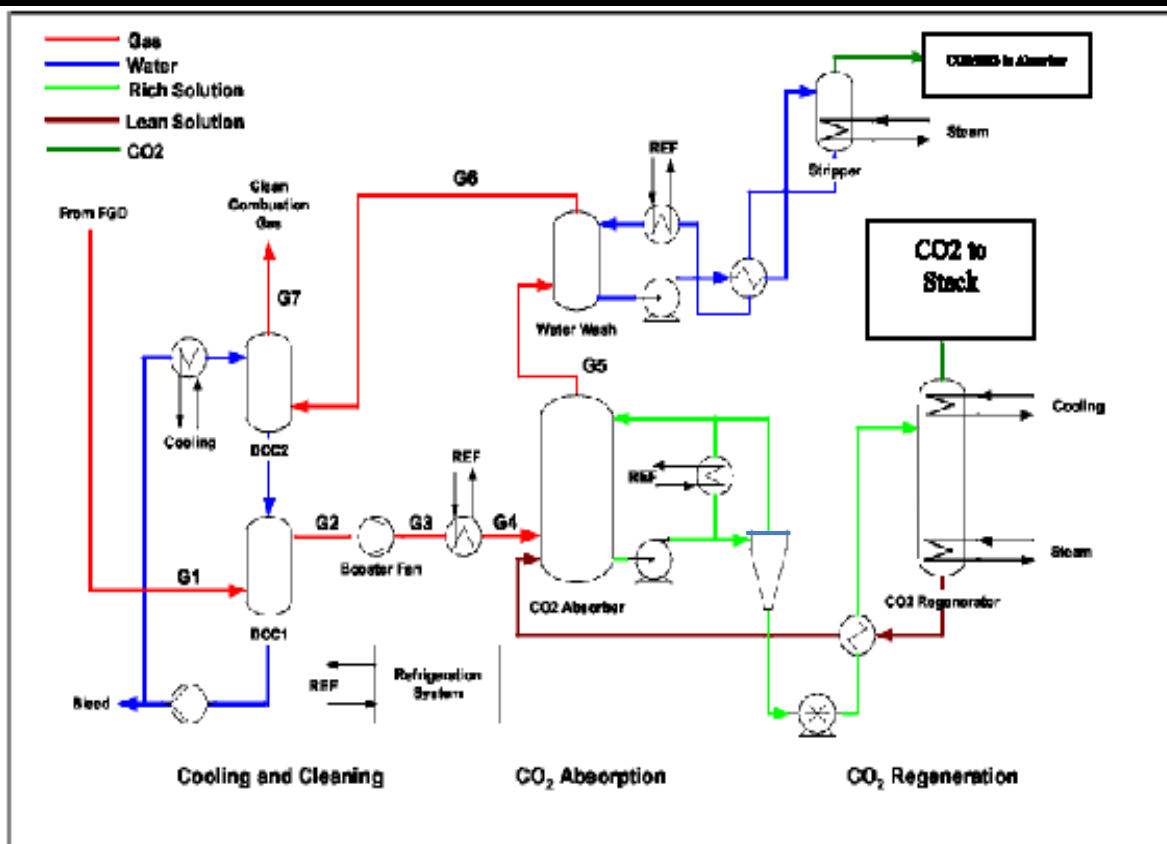
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Slide 7 shows the breakdown on the parasitic power used in each of the post combustion CC processes compared to each other. The green range (top) of power loss is attributed to the steam used in regenerating the CAP solvent. Clearly the green range is less than both Econamine FG and KM CDR.

The red section (middle) of the power loss of the Alstom's parasitic bar is attributed to the CO₂ compression power, also is clearly less than the other two processes.

The big difference is shown in the amount of auxiliary power required by Alstom's CAP process (the blue region – bottom - of the parasitic power loss bar).

Alstom Chilled Ammonia Process (CAP)



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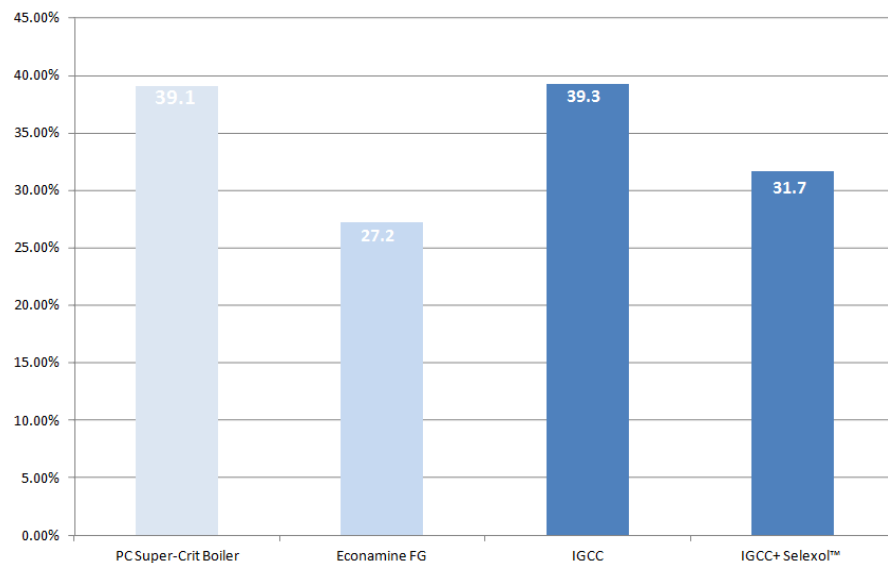
Slide 8 is a flow sheet of Alstom's process, as used in the test "Proof of Concept" demonstration facility at the Pleasant Prairie Power Plant ("P4 Plant"), in Wisconsin. This demonstration has now been discontinued and it did not compress the released CO₂ from the CO₂ stripper to super-critical pressure. Instead the CO₂ was discharged at stripper pressure (about 300 psig) into the atmosphere. The flow sketch does not show the remaining 3 stages of CO₂ compression needed to compress the CO₂ to super-critical pressure that would be needed in a commercial Alstom CAP plant.

What is apparent from the flow sheet is the amount of auxiliary equipment needed to pre-treat the flue gas, to cool the flue gas to absorption temperature, and the amount of equipment needed to recover the ammonia that would otherwise be lost to the environment. Also, a booster blower is needed to force the flue gas through all the extra towers needed in the CAP process, compared to the other two

processes evaluated. All this equipment adds both CAPEX and also parasitic power consumption. The overall result, unfortunately, does not seem to be an improvement over the KM CDR process, which uses a less efficient solvent, but without all the pretreatment equipment and power parasitic losses.

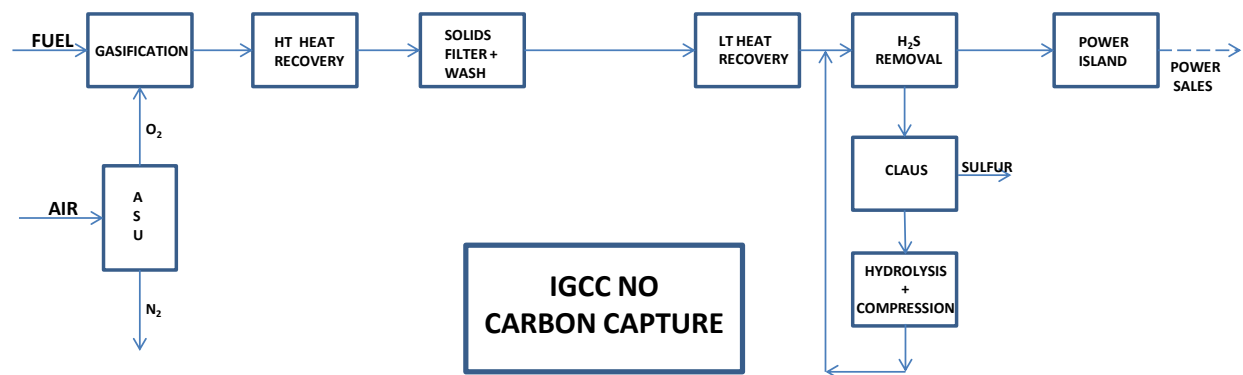
The Alstom's CAP may well develop an improvement in its technology to minimize the auxiliary power loss. Also, we can speculate that these auxiliary losses are larger in hot, humid climates, such as the Gulf Coast and the SE coast, while cool, dry northern states would have a relatively lower parasitic power penalty.

DOE/NETL Comparative Efficiency Study 2007



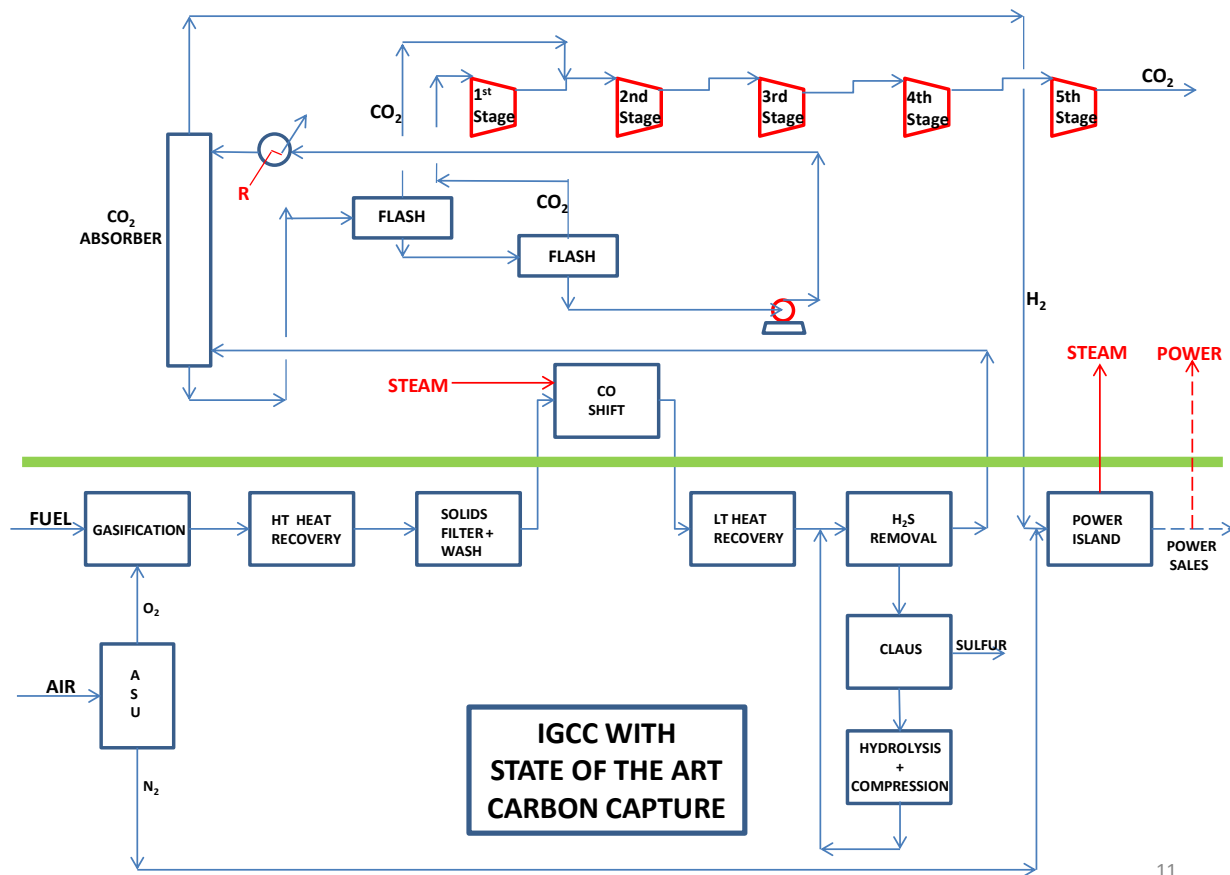
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Slide 9 Is a transition slide to now focus on the starting point of the New Pre-combustion CC processes.



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Slide 10 is a typical simplified IGCC process without CC. It features a Hydrolysis and compression process for the Claus tail gas recycle to co-feed the Acid Gas Removal (AGR) plant. This arrangement is less expensive than building a Claus Tail Gas Unit (TGU) and also it results in a 100% of the sulfur removed in the Claus plant.



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Slide 11 shows the additional process equipment needed for Pre-combustion CC following coal/coke gasification. Equipment consuming steam and power from the power island, used to power the CC process are shown in red, and represent the parasitic loss of power attributed to the Pre-combustion CC.

The generic process is typical for the DEPG (Selexol) type solvent and the methanol (Rectisol) solvent.

Usually the CO-Shift process is inserted after the solids removal and synthesis gas wash step, and upstream of the Low Temperature (LT) heat recovery section. The downstream H₂S removal step is required to selectively remove the H₂S in the presence of a large partial pressure of CO₂. The selectivity of the solvent is crucial to minimize the co-absorption of CO₂ at this stage of the process. The two competing solvents have different abilities for selective H₂S absorption, requiring different processing schemes to achieve comparable selectivity. In the remainder of the process, the CO₂ is then absorbed in the absence of H₂S and is flash regenerated in several stages. One stage of flash is typically above atmospheric pressure and one at about atmospheric pressure. If more flash stages are required, then there may be a sub-atmospheric flash required.

The compression of CO₂ to super-critical pressure is then accomplished in 5 stages, without the need for H₂O removal (dehydration). The power parasitic losses occur due to the need for steam to cause the CO Shift reaction, and due to the power needed to compress the CO₂ to super-critical pressure.

Pre-Combustion Carbon Capture

Basis: 90% CO₂ Capture

- State of the art: Selexol™ Vs. Rectisol®
- Conventional wisdom states that:
 - Selexol™ Smaller piece count = smaller CAPEX
 - Selexol™ Warmer solvent temp (0° F) Vs. Rectisol® (-70° F) = smaller OPEX for Selexol™

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Slide 12 compares the DEPG process versus the Rectisol process following Coal gasification, in which the H₂S is completely removed following the CO- Shift reaction and the CO₂ is required to be captured and compressed from the synthesis gas by at least 90%.

- Conventional wisdom states that:
 - Selexol™ Smaller piece count = smaller CAPEX
 - Selexol™ Warmer solvent temp (0° F) Vs. Rectisol® (-70° F) = smaller OPEX for Selexol™

There are exceptions to conventional wisdom which will be discussed.

Physical Solvent Solubility Data

Solubility Data (Nm³ Gas/m³ Liquid)

Component	DEPG (Selexol)	NMP (Purisol)	PC (Fluor Solv)	Methanol (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. ¹³

Slide 13 shows various commercial solvents capacity to absorb the H₂S and the CO₂ through physical absorption. Physical absorption requires that the partial pressure of the individual gas component to be high enough to cause the acid gas component to be absorbed by the solvent. This table was generated by running the ProMax simulation package (from Brian Research and Engineering) at the various conditions of a gas/liquid mixture in a flash operation. The acid gas component absorption rate is dependent on the partial pressure of the component in the gas phase and also the temperature of the mixture. The higher the partial pressure of the acid gas component, the higher is the capacity of the solvent to absorb more of the acid gas component. The lower the mixture temperature, the larger is the capacity of the solvent to absorb more of the acid gas component. In summary, high pressure and low temperature are helpful in minimizing solvent flow rate and equipment size.

In reviewing the selectivity below the table, we can see that DEPG and Purisol are the best solvents for the selective removal of H₂S in the presence of CO₂. The Purisol solvent has a disadvantage in that it is more volatile than DEPG, requiring additional processing steps to limit solvent loss to the synthesis gas

stream being processed. The DEPG solvent is about twice as effective as methanol for the selective removal of H₂S in the presence of CO₂. The solvent of choice for the selective removal of H₂S is DEPG

Next, look at the capacity of each of the solvents to absorb the CO₂. Here methanol is the most effective solvent for CO₂ absorption, with over 3 times the effectiveness compared to DEPG.

Auto refrigeration is experienced by all physical solvents when the acid gas is released at lower pressure. The lower solvent rate will result in a higher temperature drop during flash regeneration, which will increase the capacity of the solvent to absorb the CO₂ in a smaller liquid solvent volume. This is great news, as the smaller circulation rate reduces equipment size and cost.

In the case of using the DEPG solvent, the auto refrigeration effect must be limited due to DEPG's increase in viscosity as the temperature drops. At about 30° F, DEPG is at the lowest practical temperature. Lower temperature will increase viscosity, reduce the heat transfer coefficient in heat exchangers and also result in decreased absorption performance on the tower packing.

Methanol has no such auto refrigeration limitation, allowing the temperature to drop to the range of -60° F to -75° F after flash regeneration. This minimizes the solvent flow rate and the volume of the synthesis gas stream, due to lower operating temperature, which in turn also results in smaller equipment sizes.

Since the auto refrigeration effect is limited for the DEPG solvent, make-up refrigeration is needed by external refrigeration, using power taken from the power sales.

These observations result in the following conclusions:

Observations

- DEPG is the favored solvent for H_2S selective removal
- The DEPG and Claus plant are less expensive when H_2S is removed upstream from CO-Shift
- CO_2 is more effectively removed downstream from the CO-Shift using MeOH in absence of H_2S
- Both DEPG and MeOH will co-absorb CO and other components to contaminate CO_2 stream

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- DEPG is the favored solvent for H_2S selective removal
- The DEPG and Claus plant are less expensive when H_2S is removed upstream from CO-Shift
- CO_2 is more effectively removed downstream from the CO-Shift using MeOH, in the absence of H_2S

A separate observation not mentioned before, is the undesirable co-absorption of CO in all solvents -- including both DEPG and methanol. All components absorbed in the solvent along with the CO_2 are released during the flash regeneration step.



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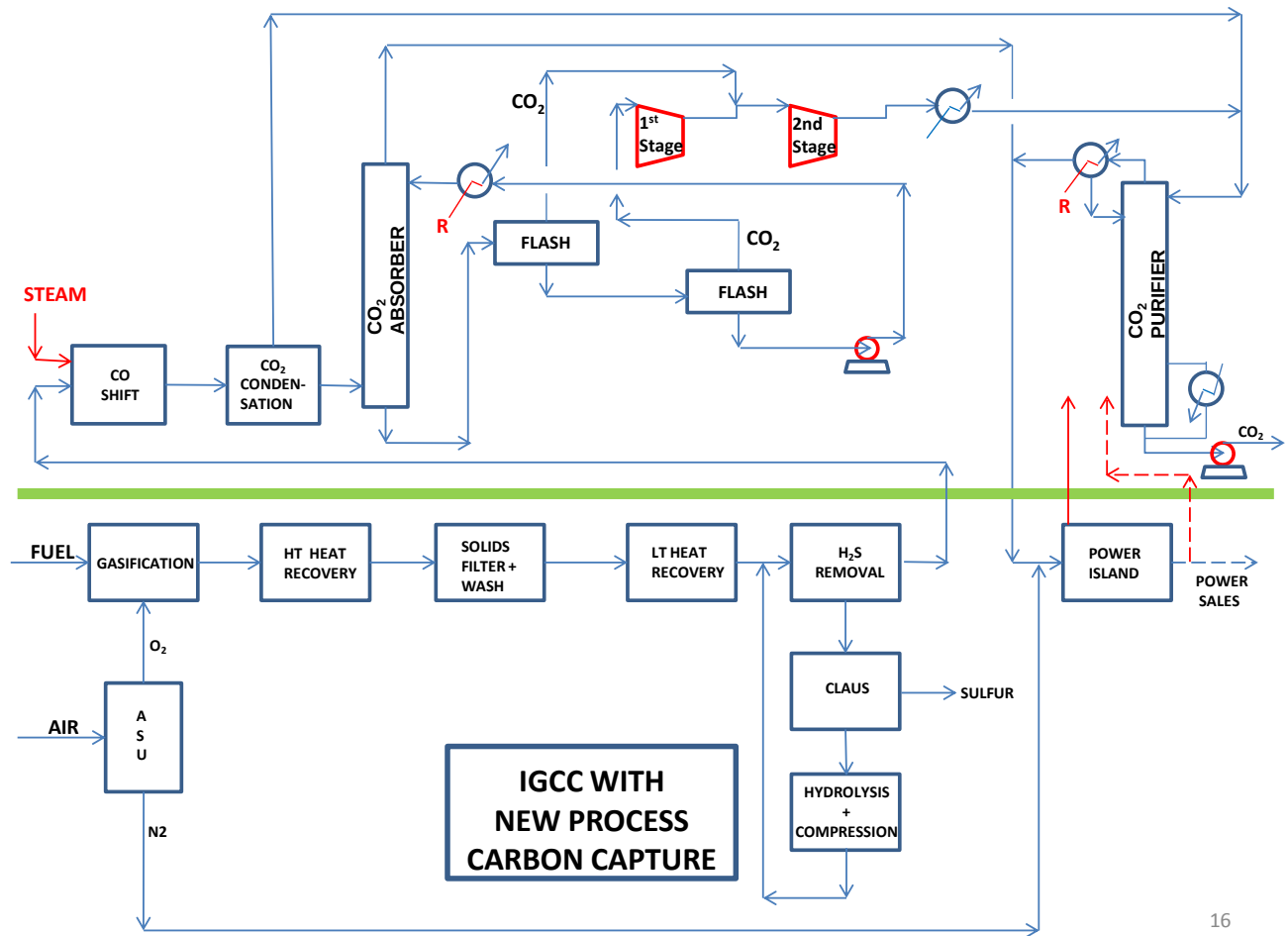
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***COMPARED TO CURRENT TECHNOLOGY - PATENT PENDING**



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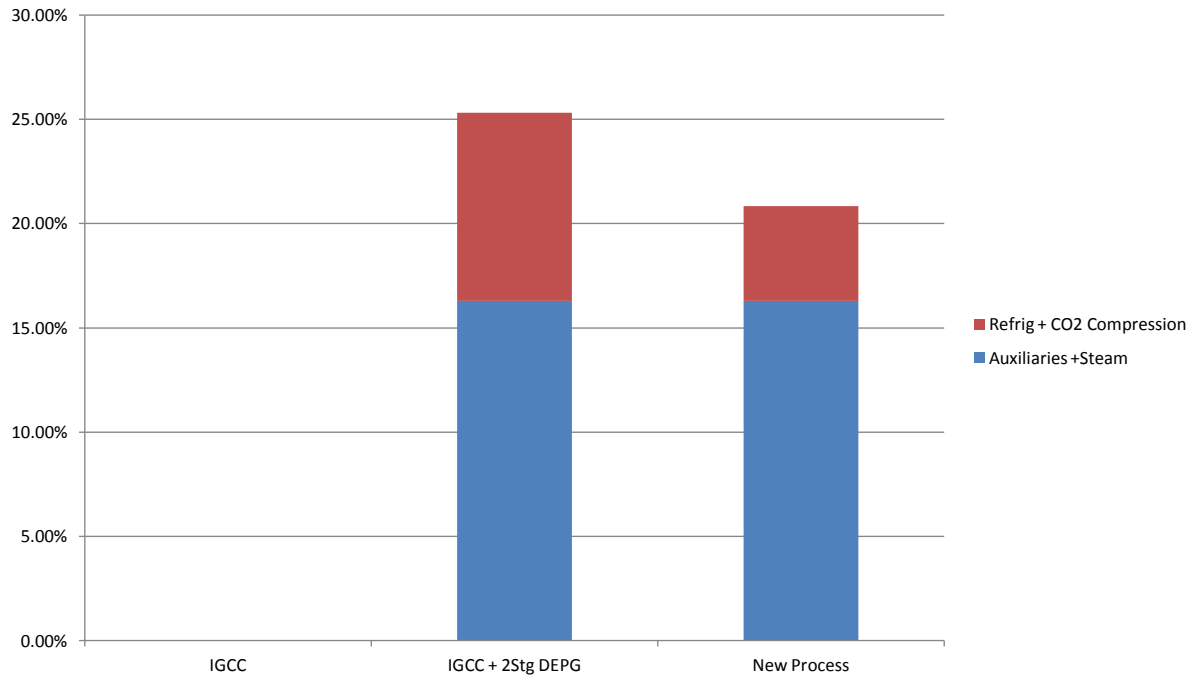
Slide 16: IGCC followed by selective removal of H₂S, via conventional DEPG (or other conventional process), followed by CO–Shift reaction and then the new CO₂ pre-combustion CC Process.

This scheme is designed to be added to an IGCC process in which the project is CC ready.

Once it is required that the IGCC project be converted to CC compliant, the new process is implemented. Then the first step of the new process condenses as much of the CO₂ as can be achieved by the partial pressure of the CO₂ in the pre-dried synthesis gas stream. Lowest temperature for condensation is limited to a few degrees above solidification of CO₂ about -69° F. Uncondensed CO₂ is then removed by a methanol absorption process. The solvent is warmed and flashed to allow for the CO₂ to be released at around 300 psig, and then the two stages of compression allow the CO₂ to condense against cooling water. The two liquid CO₂ streams are then combined together and purified in the purification distillation column.

Pure CO₂ is removed from the column bottoms and pumped to the super-critical pressure needed for transmission in the CO₂ pipeline.

Pre-Combustion CC Parasitic loss breakdown



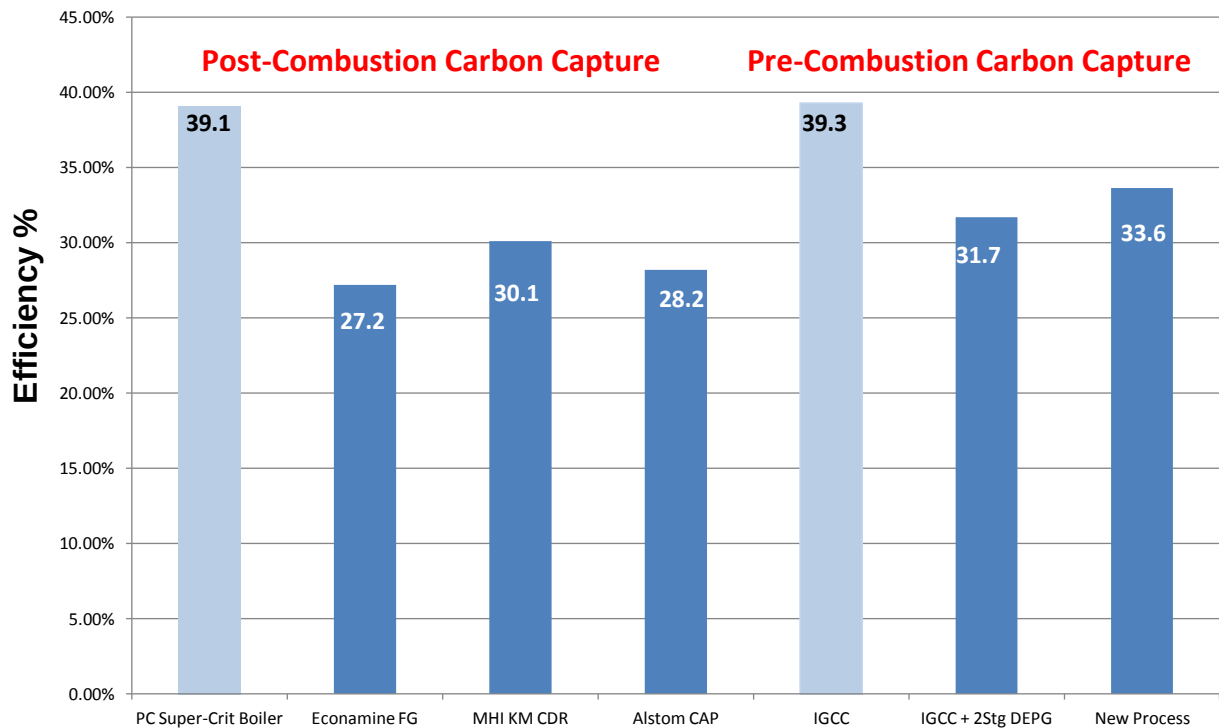
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Slide 17 shows the comparison of the new pre-combustion process against the conventional state-of-the-art process.

Power consumption in the new process is about 50% less than the conventional state-of-the-art process.

Other methods can be used to minimize the additional steam needed for the CO-Shift reaction. That is a whole separate topic for another presentation.

Comparative Summary



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Slide 18 shows the comparison of all the process in a single chart.

For post combustion CC the most efficient process is KM CDR at 30.1 %, the pre-combustion conventional 2-stage DEPG process is 31.7 %, while the new pre-combustion process is 33.6%.