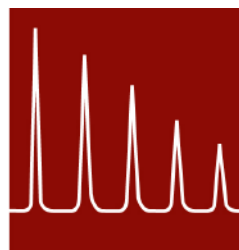


AGC NovaPRO Process Gas Chromatograph Refinery Applications

V1.0
28/03/18

AGC
INSTRUMENTS

Gas Chromatography since 1965



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Application Note #1

On-Line PGC for Crude Distillation

In the Crude Distillation Unit, the segregation of the Crude sample into narrower boiling fractions for further processing is first accomplished. Refer to Table (1) for more details.

Cut Points for the various fractions will vary, depending on the particular refinery. Most Units produce Light Ends, a De-Butanized (stabilised) 200°C endpoint straight run (SR) Naphtha, a number of intermediate distillate fractions and a heavy vacuum reduced residue.

The 200°C endpoint Naphtha is segregated as such for blending into Motor Gasoline after octane improvement by catalytic reforming. The Stabiliser removes the light ends for use in LPG and in Alkylation.

A Process Gas Chromatograph will analyse the various Analysis Points below.

Analysis Point (A)

The Stabiliser Overhead is analysed to aid in the preventing of carryover of the C5 and heavier Hydrocarbons.

Analysis Point (B)

The Bottoms product is analysed to ensure that the removal of C4 is adequate.

A Naphtha Splitter segregates the C5/C6 fraction for Octane improvement by the catalytic conversion of n-Pentane and n-Hexane to branched isomers.

Analysis Point (C)

The Bottoms product of the Splitter is monitored to ensure the complete removal of n-Hexane.

Analysis Point (D)

The Splitter Overhead is analysed to minimise the carryover of C7's and heavier.

The four analysis points at this aspect of the process have seen the sample pass through a Sample Conditioning System (SCS).

The PGC will automatically take a sample from the Process Stream via the Sample Conditioning System (SCS). Within the PGC, the sample will be separated into its individual components and after leaving the Chromatography columns, the components will pass before the Detector (typically a TCD) to measure the various levels of each component. The results will be presented within TrendVision PRO Software in a number of ways depending on what the end user prefers.

Table (1) Crude Distillation Unit Typical System Composition				
Analysis Point	(A)	(B)	(C)	(D)
	Stabiliser Overhead	Stabiliser Bottoms	Splitter Bottoms	Splitter Overhead
Inerts	2			
Methane	65			
Ethane – C2	40			
Propane – C3	5	Trace*		
Iso-Butane	3	1*		2
N-Butane	2	2*		3
Iso-Pentane	3*			25
N-Pentane			2*	15
Iso-Hexanes			2*	15
N-Hexanes				30
Cyclopentane		Balance		1
Methyl Cyclopentane				2
Cyclohexane				2
Benzene				3
C7				2*

* measured

Detailed Analysis of C2 & C7+

Ethane
 Propane
 Iso-Butane
 Butane
 Iso-Pentane
 Pentane
 Cyclo-Pentane + 2,2 Dimethyl Butane
 2 Methyl Pentane + 2,3 Dimethyl Butane
 3, Methyl Pentane
 Hexane
 Methyl Cyclopentane
 Benzene
 Cyclohexane

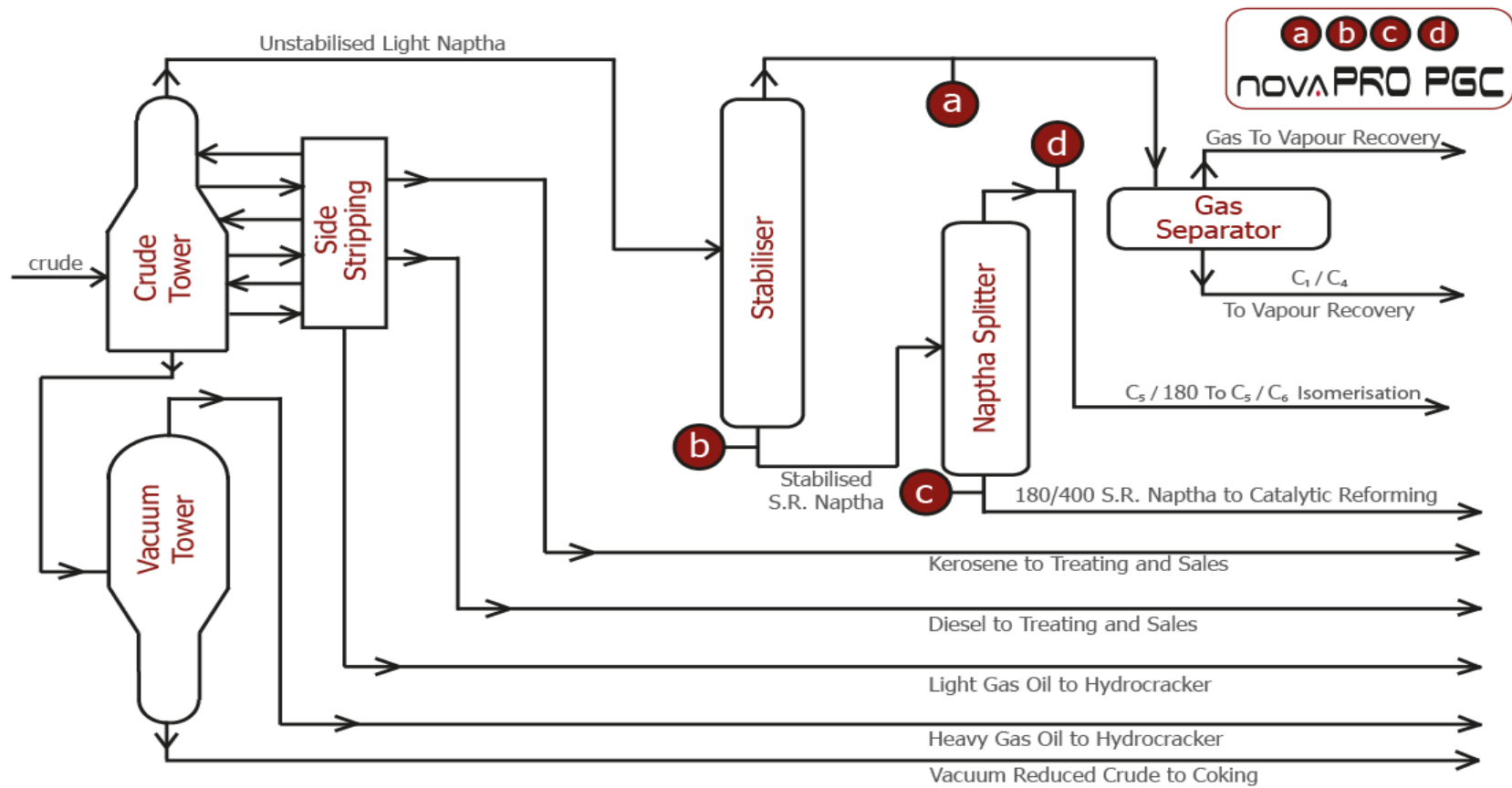
Carrier Gas:	Hydrogen
Loop Size:	0.2µl
Columns:	MXT-1 30m x 0.53mm 7DF
Analysis Time:	< 12 mins

Detailed Analysis of C4's

Propane
 N-Butane
 Iso-Butane

Carrier Gas:	Hydrogen
Loop Size:	0.5cc
Columns:	4' x 1/8" SS 10% OV101 on Chrom PAW DMCS 80/100 8' x 1/8" SS 20% OV101 on Chrom PAW DMCS 80/100
Analysis Time:	< 3 min

Crude Distillation Unit



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Application Note #2

On-Line PGC for Coking Process

Using thermal cracking in the coking process, a vacuum reduced crude produces light Hydrocarbons, gasoline and gas oil which are suitable to feed to the Catalytic Cracking Unit or the Hydrocracker. The Gasoline Stabiliser will remove the C4 and lighter to produce a stabilised 200°C endpoint motor gasoline.

There are primarily two off Analysis Points as follows:

Analysis Point (A)

A Process GC is used to monitor the composition of the Stabiliser Overhead product at this point to minimise the carryover of the C5 & heavier gasoline product.

Analysis Point (B)

Another Gas Chromatograph can be used to measure C4 and lighter components in the De-Butanised Bottoms product at Point (B).

Table (1) below will show the composition analysis as performed by the PGC's.

Table (1) Coking Typical System Composition		
Analysis Point	(A)	(B)
	Stabiliser Overhead	Stabiliser Bottoms
Hydrogen		
Methane	1	
Ethane	5	
Ethylene	1	
Propane	15	
Propylene	10	
Butane	10	1*
N-Butane	25	2*
Butylenes	30	2*
Hydrogen Sulphide	5*	Balance
* measured	3*	

The following is the Order of Elution of the components as detected by the PGC

Detailed Analysis of C4 & C5+

Propane – C3

Propylene – C3

Iso-Butane – C4

Butane – C4

1-Butene & Iso-Butylene

T2-Butene

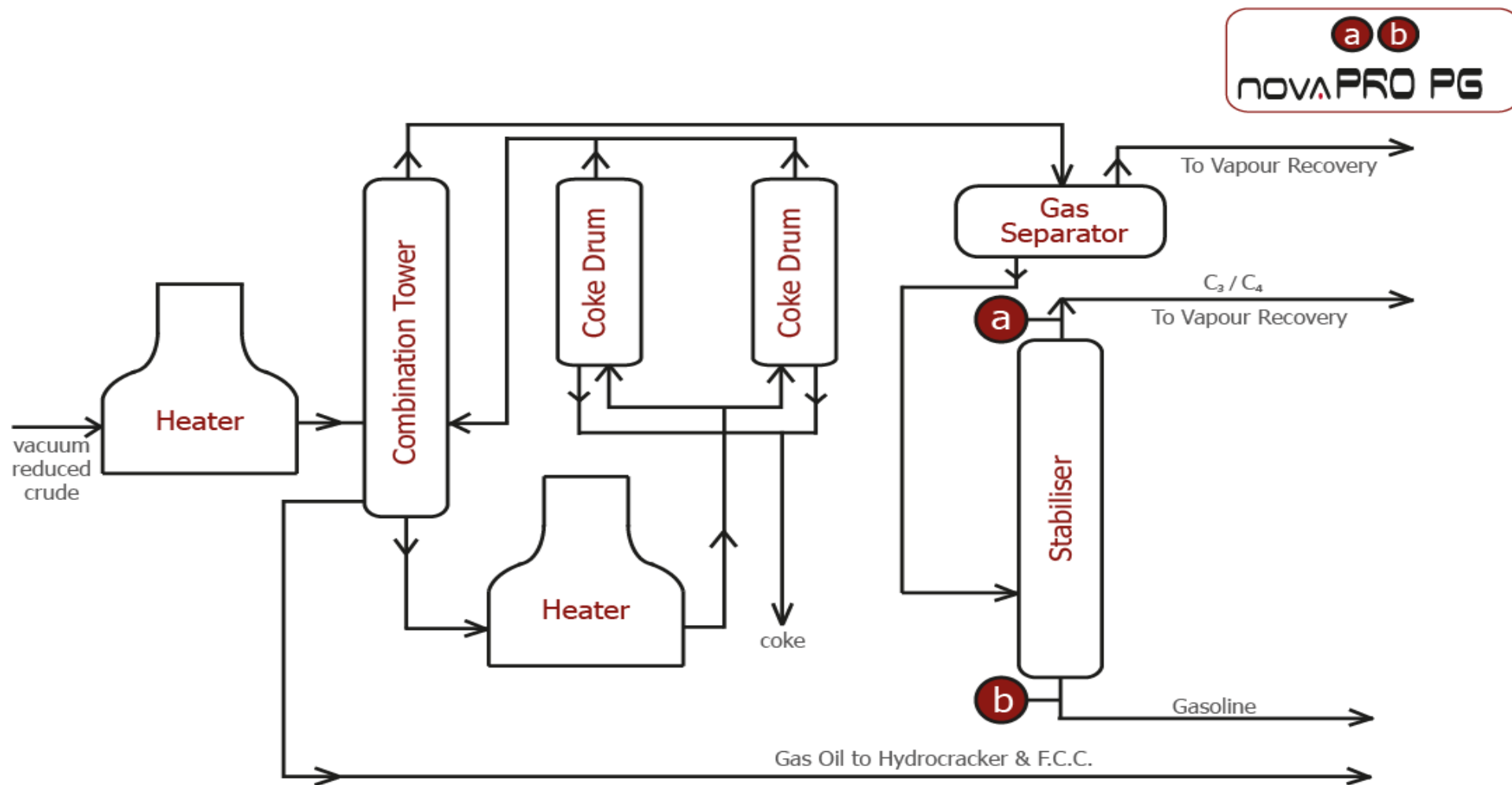
C2-Butene

1,3 Butene

C5+

Analysis Time:	< 7 mins
Carrier Gas:	Hydrogen
Loop Size:	2µl
Columns:	30m x 0.53mm MXT-1 7DF

Coking Unit



Application Note #3

On-Line PGC for Hydrocracking Unit

Hydrocracking is a more recently developed part of the refining process. It enhances gasoline production in the modern refinery and gives a wider choice of products. It is a very flexible system as it has the ability to accept feed of nearly any boiling range and can make a product at nearly any requested end point. All the heavier products are recycled to extinction.

The 200°C heavy Naphtha product also makes a very good catalytic reformer feed. In addition, Hydrocracking can be used to treat catalytic cracking feed to reduce the Sulfur & Nitrogen content.

The accompanying overview displays a two stage Hydrocracking Unit. In the first stage, the Catalytic Cracking feed stock is treated. In the second stage, it is here that both light and heavy Naphthas plus Jet Fuel are produced from a variety of feedstocks, including catalytic cracking cycle oil. The Stabiliser will remove the light ends from the C5/C6 light Naphtha.

There are Five (5) Analysis Points:

Analysis Point (A)

A Process Gas Chromatograph can be used to achieve an efficient operation of the Stabiliser as it monitors the De-Butanised C5/C6 bottoms product for residual C4's.

Analysis Point (B)

At this point, the liquid C3/C4 fractions of the Overhead can be monitored to minimise the C5 & Heavier carryover.

Analysis Point (C)

The Hydrogen content of the Make-Up and Recycle Streams must be known in order to control the ratio of Hydrogen to feed the proper value to the process. Using a PGC, the Hydrogen content of the Make-Up Hydrogen can be a blend of Hydrogen plant product and the Catalytic Reformer product gas.

Analysis Point (D) & (E)

The same PGC can also be used to measure the Hydrogen content of the Recycled Hydrogen from the High Pressure Separators. The accuracy of the Hydrogen measurement at this concentration is $\pm 1\%$.

The table below shows the composition analysis as performed with the various Process GC's.

Table (1) Hydrocracking Unit Typical System Composition				
Analysis Point	(A)	(B)	(C)	(D) & (E)
	Stabiliser Bottoms	Overhead Liquid	Make-Up Hydrogen	Recycle Hydrogen
Hydrogen			85*	80*
Methane			14	16
Ethane		7	1	2
Propane		20	<1	1
Iso-Butane	<1*	45		<1
N-Butane	1*	25		
Hydrogen Sulphide	98	1*		
* measured				

The Order of Elution of the various components detected is shown as follows:

Detailed Analysis of C4's

Propane – C3

N-Butane – C4

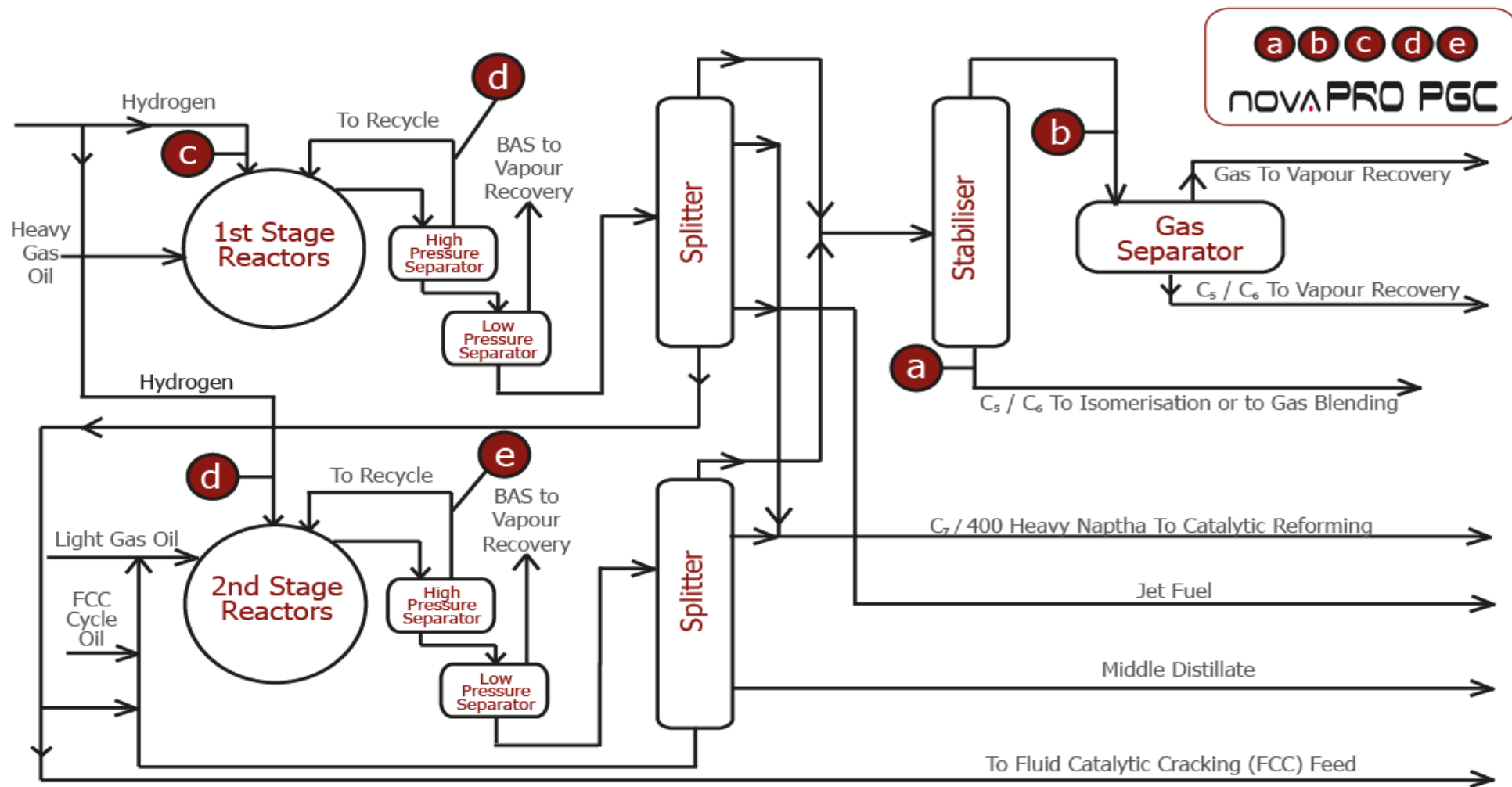
Iso-Butane – C4

Analysis Time:	< 3mins
Carrier Gas:	Hydrogen
Loop Size:	0.5cc
Columns:	4' x 1/8" SS 10% OV101 on Chrom PAW DMCS 80/100 8' x 1/8" SS 20% OV101 on Chrom PAW DMCS 80/100

The five analysis points at this aspect of the process have seen the sample pass through a Sample Conditioning System (SCS).

The PGC will automatically take a sample from the Process Stream via the Sample Conditioning System (SCS). Within the PGC, the sample will be separated into its individual components and after leaving the Chromatography columns, the components will pass before the Detector (typically a TCD) to measure the various levels of each component. The results will be presented within TrendVision PRO Software in a number of ways depending on what the end user prefers.

Hydrocracking



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Application Note #4

On-Line PGC for Catalytic Cracking Unit

Catalytic cracking has been one of the most important developments in the refining processes for converting the heavier crude oil fractions into gasoline.

Refer to the schematic that follows which is a simplified flow diagram of a fluid catalytic cracker (FCC). Feed is catalytically cracked in the reactor section to give substantially increased quantities of lighter products, including up to more than 50% conversion of 200°C endpoint gasoline and 30% of C4 and lighter. Gasoline is recovered as the bottoms product of the Stabiliser. At this point, Olefin rich C3's and C4's are removed for ultimate use in Alkylation feed. Cracked fractions heavier than 200°C can be hydrocracked to yield additional quantities of gasoline.

There are three Analysis Points

At Analysis Point (A), a Process Gas Chromatograph will aid in maintaining optimum performance of the stabiliser by monitoring the Bottoms product to ensure the adequate removal of C4's and lighter.

The Overhead product can also be monitored at Analysis Point (B) to prevent the excessive carryover of C5 and heavier hydrocarbons.

The composition of the Regenerator flue gas can be checked using a PGC at Analysis Point (C). Oxygen, Carbon Monoxide and Carbon Dioxide are usually recorded and the regeneration air rate and other conditions controlled to maintain an excess oxygen of a very low % in the flue gas. An Argon carrier gas can be used to blind out the effect of the 1% Argon that is normally present in the air. Alternatively, Helium or Hydrogen carrier gas can be used, but a constant correction to the Oxygen measurement must be made to compensate for the Argon. A typical regenerator flue gas analysis is given in Table (2) on the following page.

Compositions of the Stabiliser Overhead and Bottoms streams are similar to those indicated for the Coking Unit Stabiliser Tower.

The Composition analysis of these Analysis Points in Table (1) and (2) are performed using an on-line Process Gas Chromatograph (PGC). The PGC will automatically take a sample from the process stream via the Sample Conditioning System (SCS). This will separate the sample into its components and using the chromatography column each component elutes to be measured on the detector of the GC System. The various component concentrations are then used by the plant DCS to monitor the process unit or the fractionators performance against a given set-point.

Table (1) Catalytic Cracking Unit Typical System Composition		
Analysis Point	(A)	(B)
	Stabiliser Overhead	Stabiliser Bottoms
Inerts	2	
Methane	65	
Ethane	40	
Propane	5	Trace*
i-Butane	3	1*
N-Butane	2	2*
Iso-Pentane	3*	Balance
N-Pentane		
Iso-Hexanes		
N-Hexanes		
Cyclopentane		
Methyl cyclopentane		
Cyclohexane		
Benzene		
* measured		

Table (2) Catalytic Cracking Typical System Composition	
Analysis Point	(C)
	Regenerator Flue Gas
Oxygen	0.4*
Argon	1
Nitrogen	67
Carbon Monoxide	7.5*
Carbon Dioxide	10
Sulfur Dioxide	Trace
Water	14
* measured	

Detailed Analysis of H₂, Ar, N₂, CO₂

Hydrogen - H₂

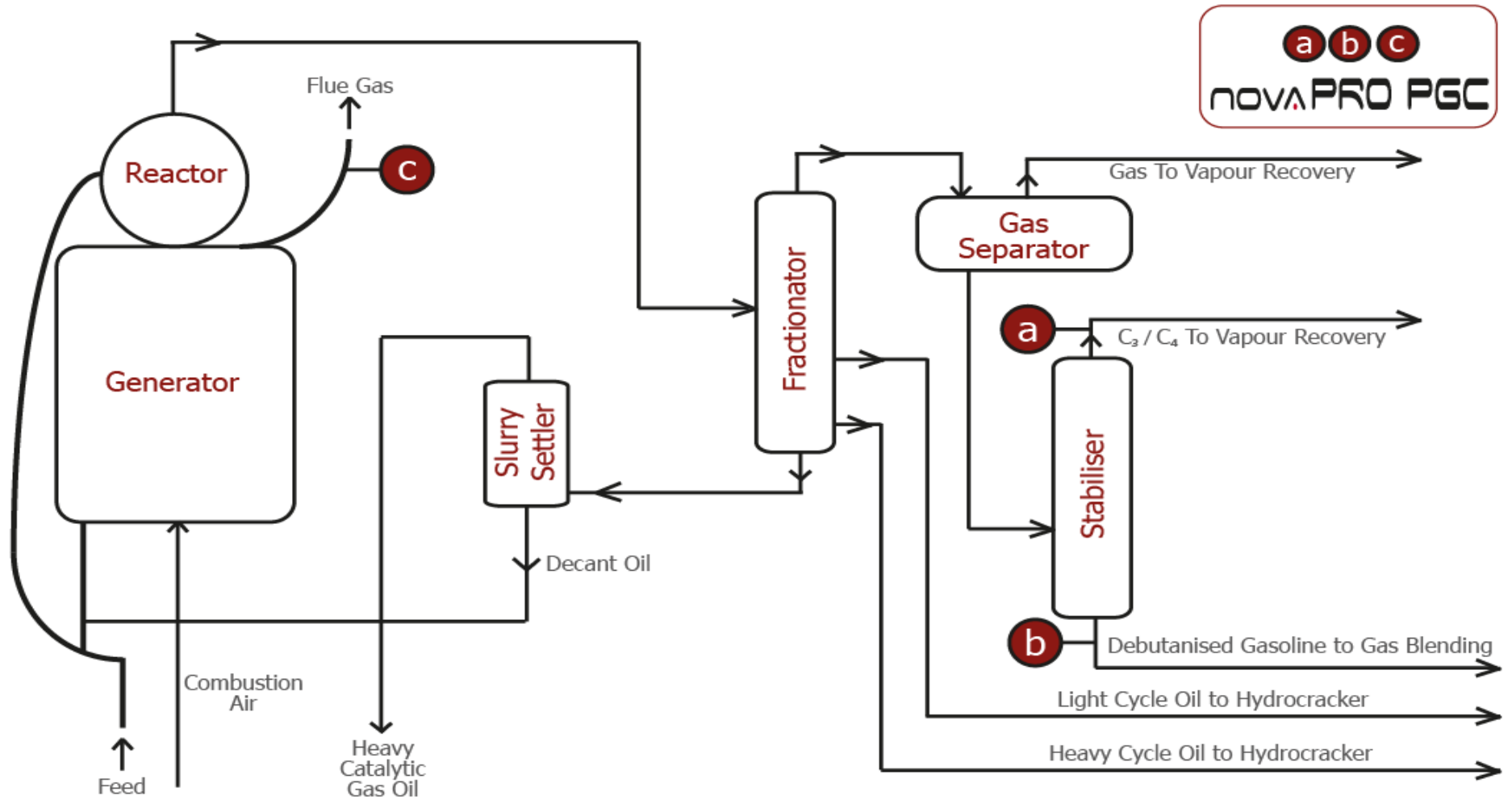
Argon – Ar

Nitrogen – N₂

Carbon Dioxide - CO₂

Analysis Time:	< 3mins
Carrier Gas:	Hydrogen
Loop Size:	0.5cc
Columns:	4' x 1/8" SS 10% OV101 on Chrom PAW DMCS 80/100 8' x 1/8" SS 20% OV101 on Chrom PAW DMCS 80/100

Catalytic Cracking



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Application Note #5

On-Line PGC for Catalytic Reforming

Catalytic reforming is widely used to upgrade low octane naphtha's to high octane gasoline by conversion of naphtha-based compounds to aromatics over a special catalyst. The main by-product is large quantities of Hydrogen. The Feed Stock is usually in the boiling range of 65°C to 200°C.

In some refineries, the feed is fractionated into an aromatic fraction and a heavy naphtha fraction and processed by the reformer in blocked out operation. High purity aromatic solvents – benzene, toluene and xylenes – can be extracted from the lighter processed fraction, while the heavier fraction is used for motor gasoline blending. A full range naphtha is sometimes processed, as in the reformer unit shown in the attached flow diagram in figure 1.

Depending on the type of catalyst and the sulphur content, a hydrodesulfurisation step may be required in the feed preparation (not described in the schematic). This usually consists of a light hydrogen treatment over catalyst to convert sulphur compounds to H₂S. The H₂S is then removed before the reforming step.

As mentioned earlier, the primary reaction in the reformer is the dehydrogenation of naphthenes to produce aromatics and hydrogen. However, some isomerisation and dehydrocyclisation of paraffins does occur. In addition, combined sulphur is converted to H₂S and substantial quantities of C1 to C4 Hydrocarbons are produced. These are removed in the Stabiliser for use elsewhere in the refinery.

The amount of light ends produced depends on the catalyst age, severity and other variables. Generally, as the catalyst ages and loses activity an increase in reactor temperature (severity) is required to maintain product quality. Increased severity usually increases the production of light ends through hydrocracking with a consequent decrease in the purity of the product and recycle Hydrogen. This in turn requires an adjustment in the Hydrogen recycle rate to control severity. Hence, continuous analysis of reformer streams is essential to maintain optimum control of the process.

Process Gas Chromatographs may be used to monitor the process at the various analysis points as indicated on the diagram.

Analysis Point (A) Hydrogen Recycle Product

Recycle Hydrogen composition at the separator can be determined with an accuracy of ±1% with the PGC using a mixed carrier gas. This value can be used to optimise the Hydrogen/Carbon ratio. Methane, Ethane and other lighter hydrocarbons can be measured simultaneously if a material balance is required.

Analysis Point (B) Unstabilised Product

At the outlet of the high pressure separator the full range of unstabilised product can be analysed at this point. In this manner, it is possible to obtain a complete analysis of the light ends as well as a total aromatics measurement of the reactor product. This latter value, when correlated with the naphthene content of the feed as determined by laboratory analysis, serves as an indicator of reactor conversion efficiency. Because of the large amounts of light ends in the sample, the chromatograph sample valve must operate at a sample pressure in excess of 500psig to prevent partial vaporisation.

Analysis Point (C) Stabilised Product

Alternatively, this measurement can be made on the stabilised reformate. Measurement at this point also permits monitoring of the stabiliser efficiency.

Analysis Point (D) Stabiliser Overhead Gas Product

A PGC also monitor the stabiliser overhead to minimise loss of product to that stream

Table (1)				
Catalytic Reforming				
Typical System Composition				
Analysis Point	(A)	(B)	(C)	(D)
	Recycle Hydrogen	Unstabilised Product	Stabilised Product	Stabiliser Overhead Gas
Hydrogen	80*	Trace		10
Methane	12**	<1*		30
Ethane	5**	<1*		20
Propane	2**	1*		20
Iso-Butane	1**	2*	<1	10
N-Butane	<1	2*	1	10
C5+ non Aromatics		45	44	
Aromatics		50**	54**	4*
* measured				
** optional				

Detailed Analysis of C4 & C5+

Propane – C3

Propylene – C3

Iso-Butane – C4

Butane – C4

1-Butene & Iso-Butylene

T2-Butene

C2-Butene

1,3 Butadiene

C5+

Analysis Time:	< 7 mins
Carrier Gas:	Hydrogen
Loop Size:	2µl
Columns:	30m x 0.53mm MXT-1 7DF

Detailed Analysis of C5's

Methane – C1

n-Butane – n-C4

Ethane – C2

i-Pentane – i-C5

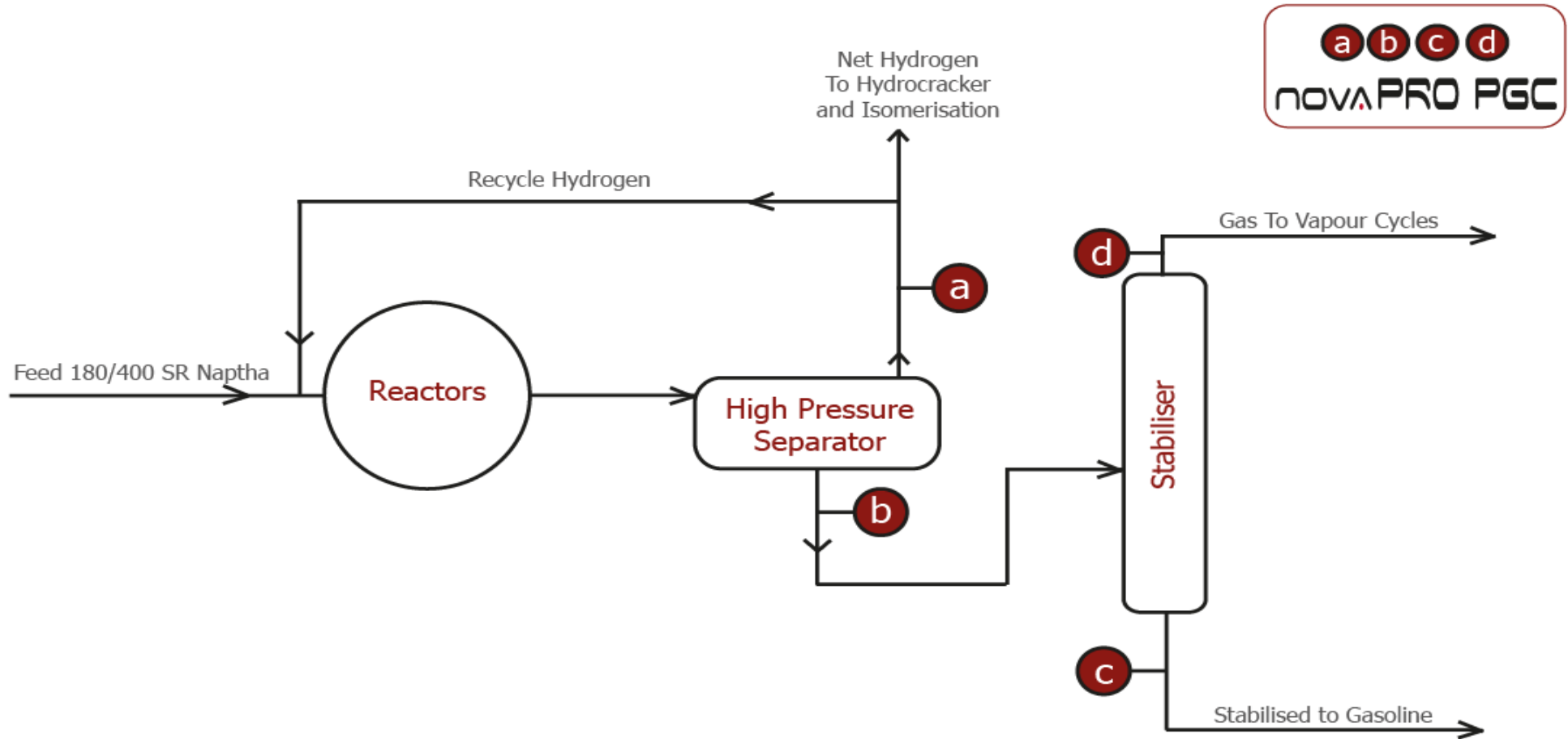
Propane – C3

n-Pentane – c-C5

i-Butane – i-C4

Analysis Time:	< 2 mins
Carrier Gas:	Hydrogen
Loop Size:	0.5cc
Columns:	20% OV-101 on Chrom PAWDMCS 80/100 Col 1 = 4' x 1/8"

Catalytic Reforming



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Application Note #6

On-Line PGC for Alkylation

This process is used to produce high quality aviation and motor gasoline from light Hydrocarbons. Olefins are introduced to react with a large excess of iso-Butane in the presence of a catalyst to form highly branched Paraffins. The Catalysts typically used are Sulphuric Acid & Hydrofluoric Acid (HF) with Sulphuric Acid being the most common.

There are three common elements of the Alkylation Systems:

- (1) Reactor Section
- (2) Acid Recovery Section
- (3) Fractionation section (to separate the Alkylate product and recover the unreacted components).

The Olefin Feed consists normally of C3's and C4's and sometimes C5's. Since the Olefins originate from Thermal or Catalytic cracking, they will contain a lot of Propane (C3's) and Butane (C4's).

Process Gas Chromatographs are used widely in the Alkylation plants. Their main use is to aid in the control of the iso-Butane to Olefin ratio. The reason being that it is necessary to know the Olefin and iso-Butane content of all streams entering the reactor.

The PGC will measure the Propylene and total Butylenes in the Olefin feed stream which is done at Analysis Point (A). The TrendVision PRO Software will sum the four Butylenes isomers to give a single reading. Iso-Butane can also be measured in this stream. This is not a necessary reading as it is only present in a small amount compared to the large amount added as recycle.

n-Butane content is measured at Analysis Point (C) by a PGC. The n-Butane must be kept at an optimal level so the operation of the deiso-butaniser is adjusted to maintain this.

Similarly, the n-Butane at Analysis Point (D) which is the feed to the Isomerisation plant is monitored so that the iso-butane content in that stream is minimised.

The Overhead and Bottoms streams are analysed by the Gas Chromatograph. This allows the depropaniser operation to be optimised. As iso-Butane is more valuable as alkylate than as LPG, its value is monitored in the overhead of the depropaniser which is Analysis Point (E).

Tower operation should be trimmed to minimise the propane content in the bottoms product, and monitoring of this is done at Analysis Point (F).

Analysis Points (G) and (H) are the monitoring points for the incoming mixed Butanes streams and are required for the operation of the isobutaniser tower. In some plants, this Butane stream is fed direct to the reactors. When this happens, a PGC analysis is totally necessary to control the iso-Butane/Olefin ratio.

Alkylation Unit Typical System Composition							
Analysis Point	(A)	(B)	(C)	(D)	(E)	(F)	(G) & (H)
	Olefin Feed	Deiso-butaniser		N-Butane Sidecut	Depropaniser		Mixed Butanes
		Overhead	Bottoms		Overhead	Bottoms	
Ethane	Trace				1		
Propane	15	2			98	4*	2
Propylene	20*						
Iso-Butane	20**	95	1	6*	1*	95	48*
N-Butane	15	3*	4*	90		1*	48
Butylenes	30*						
C5+	Trace	Trace	95	4*			2
* measured							
** optional							

The PGC will automatically take a sample from the Process Stream via. Within the PGC, the sample will be separated into its individual components and after leaving the Chromatography columns, the components will pass before the Detector (typically a TCD) to measure the various levels of each component. The results will be presented within TrendVision PRO Software in a number of ways depending on what the end user prefers.

Detailed Analysis of C4 & C5+

Propane – C3
 Propylene – C3
 Iso-Butane – C4
 Butane – C4
 1-Butene & Iso-Butylene
 T2-Butene
 C2-Butene
 1,3 Butadiene
 C5+

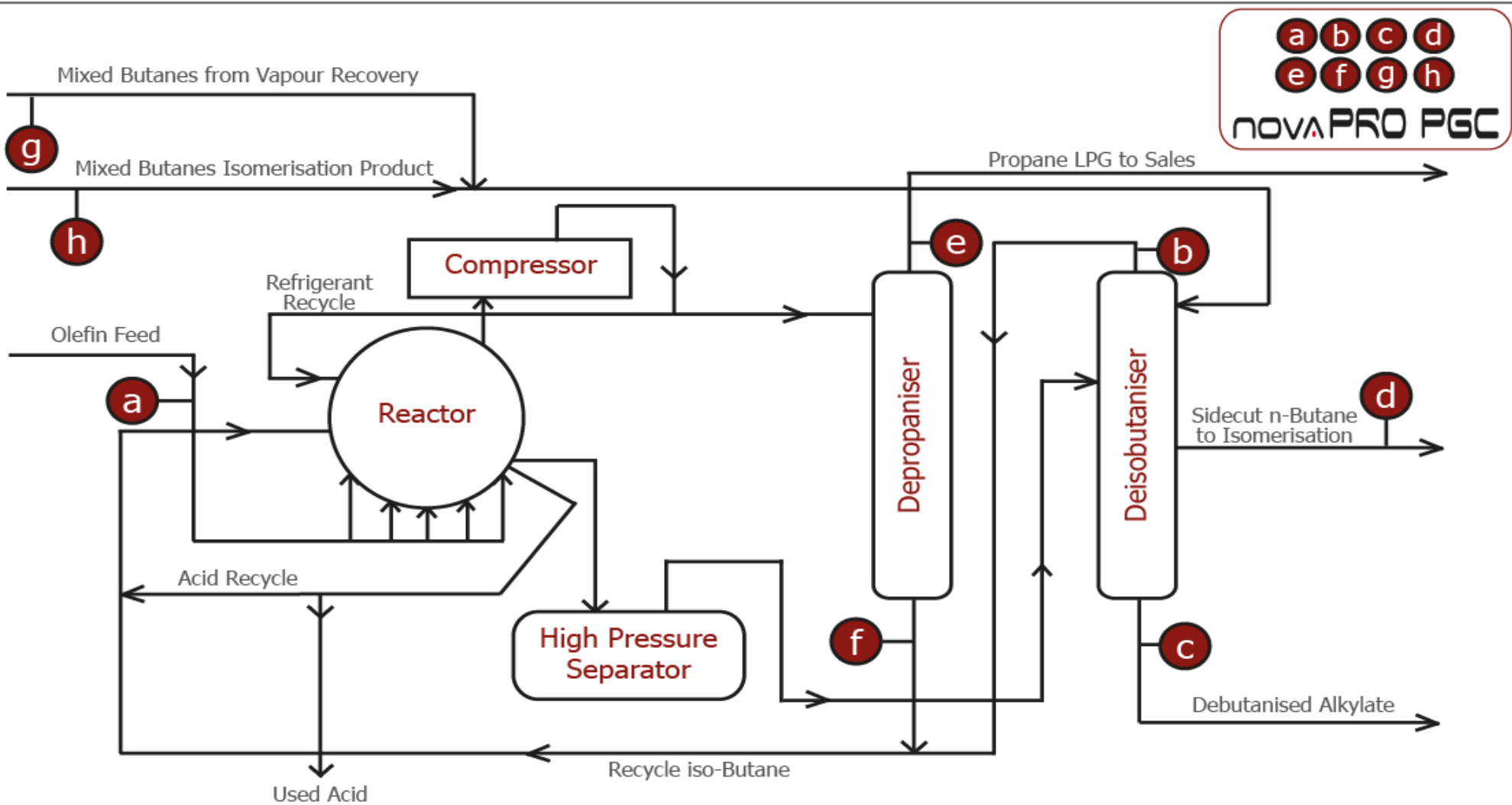
Analysis Time:	< 7 mins
Carrier Gas:	Hydrogen
Loop Size:	2µl
Columns:	30m x 0.53mm MXT-1 7DF

Detailed Analysis of C4's

Propane – C3
 n-Butane – C4
 i-Butane

Analysis Time:	< 2 mins
Carrier Gas:	Hydrogen
Loop Size:	0.5cc
Columns:	20% OV-101 on Chrom PAWDMCS 80/100 Col 1 = 4' x 1/8" Col 2 = 8' x 1/8"

Alkylation



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Application Note #7

On-Line PGC for Butane Isomerisation

The butane isomerisation process is one where the n-butane is converted to iso-butane for use in the Sulphuric or HF alkylation. If sufficient iso-butane is not available from natural gasoline stocks or from other sources to meet alkylation, it usually required.

As shown in the process in Figure 1, the liquid n-butane concentrate is contacted with an HCl-promoted liquid catalyst to allow a partial conversion to iso-butane. This is done under moderate heat and pressure. As a pre-treatment of the n-butane concentrate, it may be required to remove the iso-pentane and heavier in the debutaniser distillation tower. The C5's tend to crack into lighter hydrocarbons (disproportionation) as a side reaction in the process. These are undesirable components.

The iso-butane product will consist of equal portions of iso-butane and n-butane (approximately). The HCl tower will remove the HCl; the product is then neutralised and water-washed as a final step in the process.

Using Gas Chromatographic analysis at the various points shown in the flow diagram, an efficient operation can be obtained.

Analysis Point (A)

This serves to monitor the quality of the feed to the process. It is necessary to minimise the iso-butane, the iso-pentane and heavier components in this stream. Excess iso-butane in the feed will suppress the conversion while the C5's will form the lighter compounds as stated earlier.

Analysis Point (B)

At this point the efficiency of the debutaniser can be monitored for n-butane at the Bottoms product.

Analysis Point (C)

The overhead product also needs to be analysed for iso-pentane and n-butane content. By comparing the latter measurement with that of the n-butane in the product, a direct indication of conversion can be obtained.

Removal of HCl from the product is done in the HCl removal tower. An efficient operation is essential to prevent carryover of the HCl and to minimise the caustic consumption in the treaters.

Analysis Point (D)

Any residual HCl in the bottoms product of this unit can be measured by a Gas Chromatographic method. A specially prepared column is required for HCl as it is a difficult component to separate. N-butane can also be measured at this point to enable the determination of the conversion efficiency.

Analysis Point (E)

Alternatively, conversion can be determined by measuring the n-butane content of the product after the treaters

Table (1) Butane Isomerisation Typical System Composition					
Analysis Point	(A)	(B)	(C)	(D)	(E)
	Plant Feed	Debutaniser		HCl Removal Bottoms	N-Butane Product
		Bottoms	Overhead		
HCl				<1*	
C2's				Trace	Trace
C3's	Trace		Trace	Trace	Trace
i-butane	6		6	55	55
n-butane	90*	2*	94	34*	45*
i-pentane	4	98	<1*	<1	<1
*measured					

The analysis of these points in Table (1) above is performed using an on-line Process Gas Chromatograph (PGC). The PGC will automatically take a sample from the process stream via the Sample Conditioning System (SCS). This will separate the sample into its components and using the chromatography column each component elutes to be measured on the detector of the GC System. The various component concentrations are then used by the plant DCS to monitor the process unit or the fractionators performance against a given set-point.

Detailed Analysis of C4's

Propane
n-Butane
i-Butane

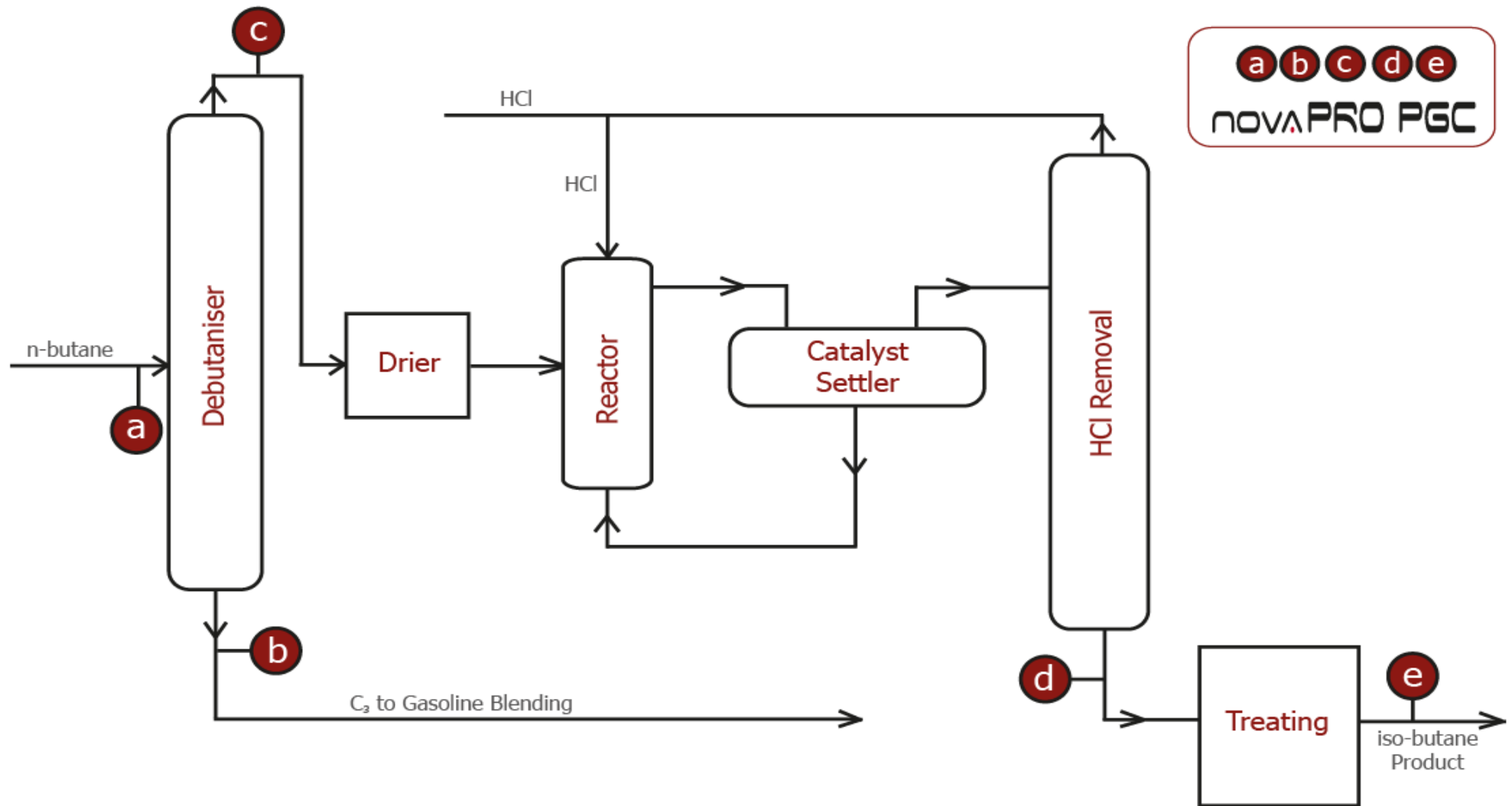
Analysis Time: < 3 mins
Carrier Gas: Hydrogen
Loop Size: 0.5cc
Columns: 4ft x 1/8" 10% OV101 on Chrom PAW DMCS 80/100
8ft x 1/8" 10% OV101 on Chrom PAW DMCS 80/100

Detailed Analysis of C4's & C5+

Propane
Propylene
Iso-Butane
Butane
1-Butene & Iso-Butylene
T2-Butene
C2-Butene
1,3 Butadiene
C5+

Analysis Time: < 7 mins
Carrier Gas: Hydrogen
Loop Size: 2µl
Columns: 30m x 0.53mm MXT-1 7DF

Butane Isomerisation



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Application Note #8

On-Line PGC for Pentane/Hexane Isomerisation

Pentane/Hexane Isomerisation is used to improve the Octane rating during the C5/C6 natural gasoline fraction.

In the process as outlined in Table (1), n-pentane & n-Hexane are converted to iso-pentane & iso-hexanes by being passed over a special catalyst. This is an equilibrium reaction and the conversion of pentane is done by taking the incoming feed and removing the iso-pentane within the deisopentaniser distillation column. At the same time, this column will remove the iso-pentane product from the recycle stream. The Iso-pentane overhead is later combined with the hexane product.

Hydrogen is mixed in Deisopentaniser bottoms and under high pressure and temperatures up to 200°C, and fed to the reactor. At this point the normal paraffins undergo isomerisation to branched compounds. The cyclic compounds are converted to paraffins or brought to equilibrium with each other. Benzene is hydrogenated to cyclohexane. C4 and lighter compounds formed along with dissolved Hydrogen are removed in the stabiliser column.

An HCl promoted catalyst as used in other similar processes requires the addition of HCl to the reactor feed. At this point additional HCl recovery equipment is also required.

Analysis Point (A) & (B)

By using Process Gas Chromatographs, optimum efficiency can be gained at various points. For example, the deisopentaniser operation should be optimised around the iso-pentane & n-pentane separation by having the minimum amount of n-pentane in the overhead at Analysis Point (A) and of iso-pentane in the bottoms product at Analysis Point (B).

Analysis Point (C) & (D)

A PGC is also used to get the best operation of the C5/C6 splitter by measuring cyclopentane or 2,2 dimethylbutane (2,2-DMB) in the overhead at Analysis Point (C). The boiling point of cyclopentane is very close to or is slightly lower than the 2,2 dimethylbutane (2,2-DMB). By ensuring that the cyclopentane is kept to a minimum in the overhead, this will ensure that the iso-hexanes are kept in the bottoms product. At Analysis Point (D), the n-pentane in the bottoms needs to be measured. The tower needs to be maintained to minimise the amount of the n-pentane remains in the bottoms product.

Analysis Point (E)

The Hydrogen content of the hydrogen recycle stream has to be maintained to with $\pm 0.1\%$ and this where a gas chromatograph is utilised again.

The analysis of these points in Table (1) is performed using an on-line Process Gas Chromatograph (PGC). The PGC will automatically take a sample from the process stream via the Sample Conditioning System (SCS). This will separate the sample into its components and using the chromatography column each component elutes to be measured on the detector of the GC System. The various component concentrations are then used by the plant DCS to monitor the process unit or the fractionators performance against a given set-point.

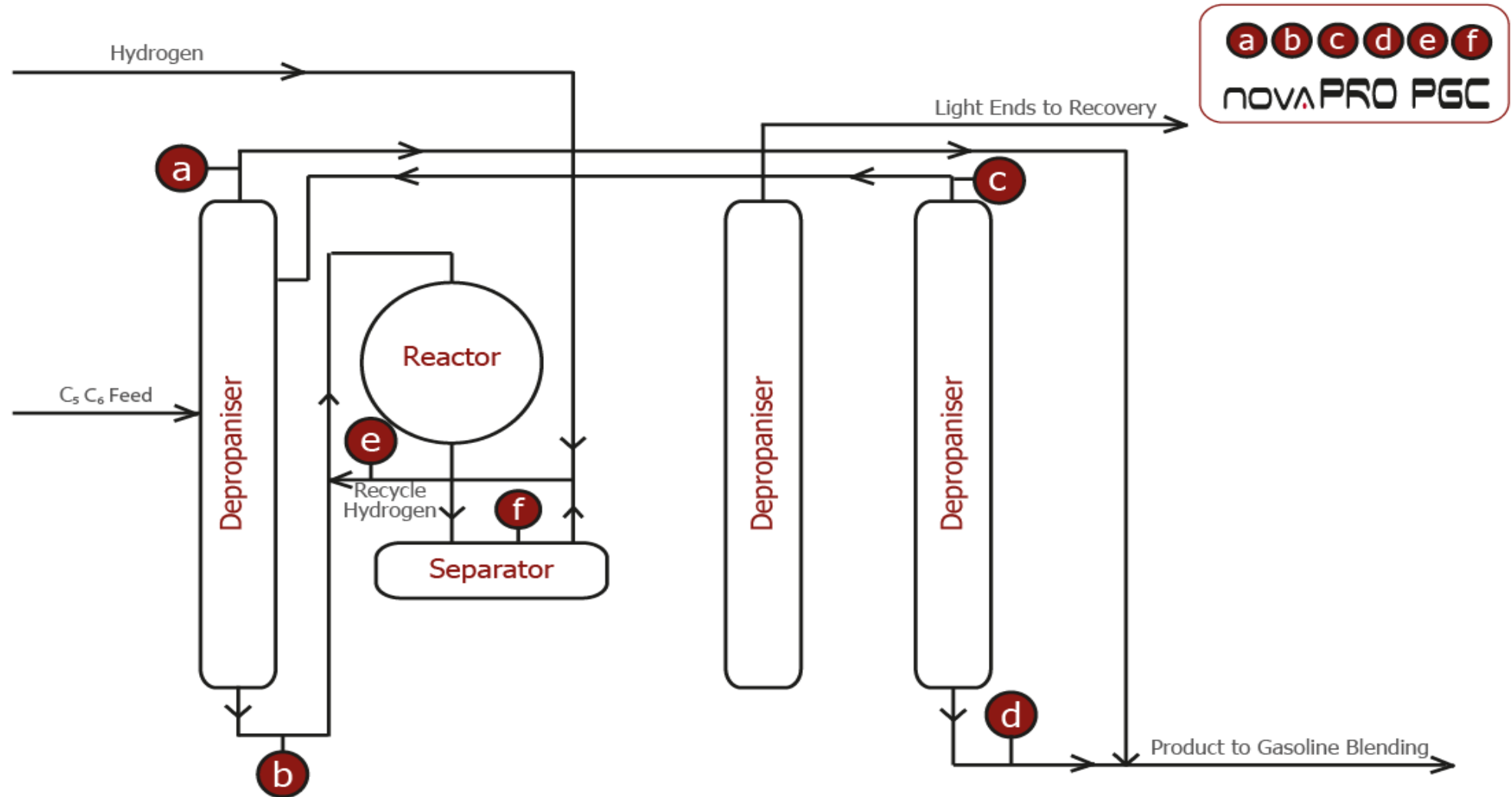
Table (1) Pentane/Hexane Isomerisation Typical System Composition					
Analysis Point	(A)	(B)	(C)	(D)	(E)
	Deisopentaniser		C5/C6 Overhead	Splitter Bottoms	Hydrogen Make-Up
	Overhead	Bottoms			
Hydrogen					97*
Methane					3
N-Butane	2		2*		
Iso-Butane	95	1*	85		
N-Pentane	3*	45	12	1*	
Cyclopentane		2	1*	2	
2,2 Dimethylbutane		1	Trace*	22	
2,3 Dimethylbutane		2		10	
2 Methyl Pentane		3		22	
3 Methyl Pentane		4		16	
N-Hexane		30		9	
Methyl Cyclopentane		4		9	
Cyclohexane		2		9	
Benzene		2			
*measured					
**optional					

Detailed Analysis of C2 & C7+

Ethane
 Propane
 Iso-Butane
 Butane
 Iso-Pentane
 Pentane
 Cyclopentane + 2,2 Dimethylbutane
 2 Methyl pentane + 2,3 Dimethylbutane
 3 Methyl pentane
 Hexane
 Methyl cyclopentane
 Benzene
 Cyclohexane

Analysis Time: < 7 mins
 Carrier Gas: Hydrogen
 Loop Size: 0.2µl
 Columns: MXT 30m x 0.53mm 7DF
 8ft x 1/8" 10% OV101 on Chrom PAW DMCS 80/100

Pentane/Hexane Isomerisation



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Application Note #9

On-Line PGC for Hydrogen Plant

Vast quantities of Hydrogen are used during the Hydrocracking processes. While the Reformer Unit will generate a lot of Hydrogen, it is only a minor amount that is required to meet normal Hydrocracking requirements. A Steam Reforming Plant/Unit can be used to generate the required quantities. Such a Steam Reformer would be similar to that found in Ammonia plants.

Refer to Schematic 1, where a typical reformer is shown. A mixture of Natural Gas & Steam is passed over a reforming catalyst to provide a mixture of Hydrogen (H_2) and Carbon Monoxide (CO). Steam is used to remove the CO by reaction with the Steam in shift convertors to give more H_2 and Carbon Dioxide (CO_2). The CO_2 is absorbed in an amine solution in the absorbers which is subsequently recovered in the absorber generator. Traces of CO and CO_2 in the H_2 product are converted to Methane (CH_4) in the Methanator.

Process Gas Chromatographs are used to maintain an efficient operation of each of the units in the process. Refer to Schematic 1 to identify the various points of analysis in the Streams.

Analysis Point (A)

The Natural Gas is analysed where the Methane (CH_4) and Ethane (C_2H_6) is essential to controlling the addition of Steam to the feed.

Analysis Point (B)

At this point, the Reformer efficiency can be monitored by analysing and quantifying the unconverted Methane at the reformer outlet.

Analysis Point (C) & (D)

By analysing these two analysis points for CO content, efficiency of the shift reaction in the shift convertors can be found out and monitored. At this stage in the process, the CO content should be a fraction of a percent (%) at the outlet of the low temperature convertor.

Analysis Point (E)

In order to attain the required H_2 purity, the efficiency of the CO_2 removal in the absorber is essential. The overall efficiency of the absorber can be determined by measuring the CO_2 content at the outlet at Analysis Point (E). By using a mixed carrier gas, the H_2 content of the process stream can be measured with an accuracy of $\pm 1\%$.

Analysis Point (F)

By monitoring the residual CO_2 in the methanator outlet product gas, the Methanator operation can be monitored. The H_2 content of the product can be measured with the same PGC if a mixed carrier gas is used. In analysing the overall plant operation, CH_4 & N_2 can be measured as an option, although it is not essential.

The analysis of these points in Table (1) is performed using an on-line Process Gas Chromatograph (PGC). The PGC will automatically take a sample from the process stream via the Sample Conditioning System (SCS). This will separate the sample into its components and using the chromatography column each component elutes to be measured on the detector of the GC System. The various component concentrations are then used by the plant DCS to monitor the process unit or the fractionators performance against a given set-point.

Table (1) Hydrogen Plant Typical System Composition						
Analysis Point	(A)	(B)	(C)	(D)	(E)	(F)
	Convertor Feed	Reformer	High Temp Shift Convertor	Low Temp Shift Convertor	Absorber Outlet	Product H ₂ Methanator Outlet
Hydrogen		40*	45	45	97*	97*
Nitrogen	Trace	Trace	Trace	Trace	Trace	Trace**
Carbon Monoxide		5	1*	Trace*	0.5*	
Carbon Dioxide	Trace	5	9	9	Trace	Nil*
Methane	87**	1*	1	1	2	2.5**
Water		50	45	45	0.5	0.5
Ethane	10*					
Propane & Heavier	3					
*measured						
**optional						

Detailed Analysis of Light Gases

Oxygen
Nitrogen
Methane
Carbon Monoxide

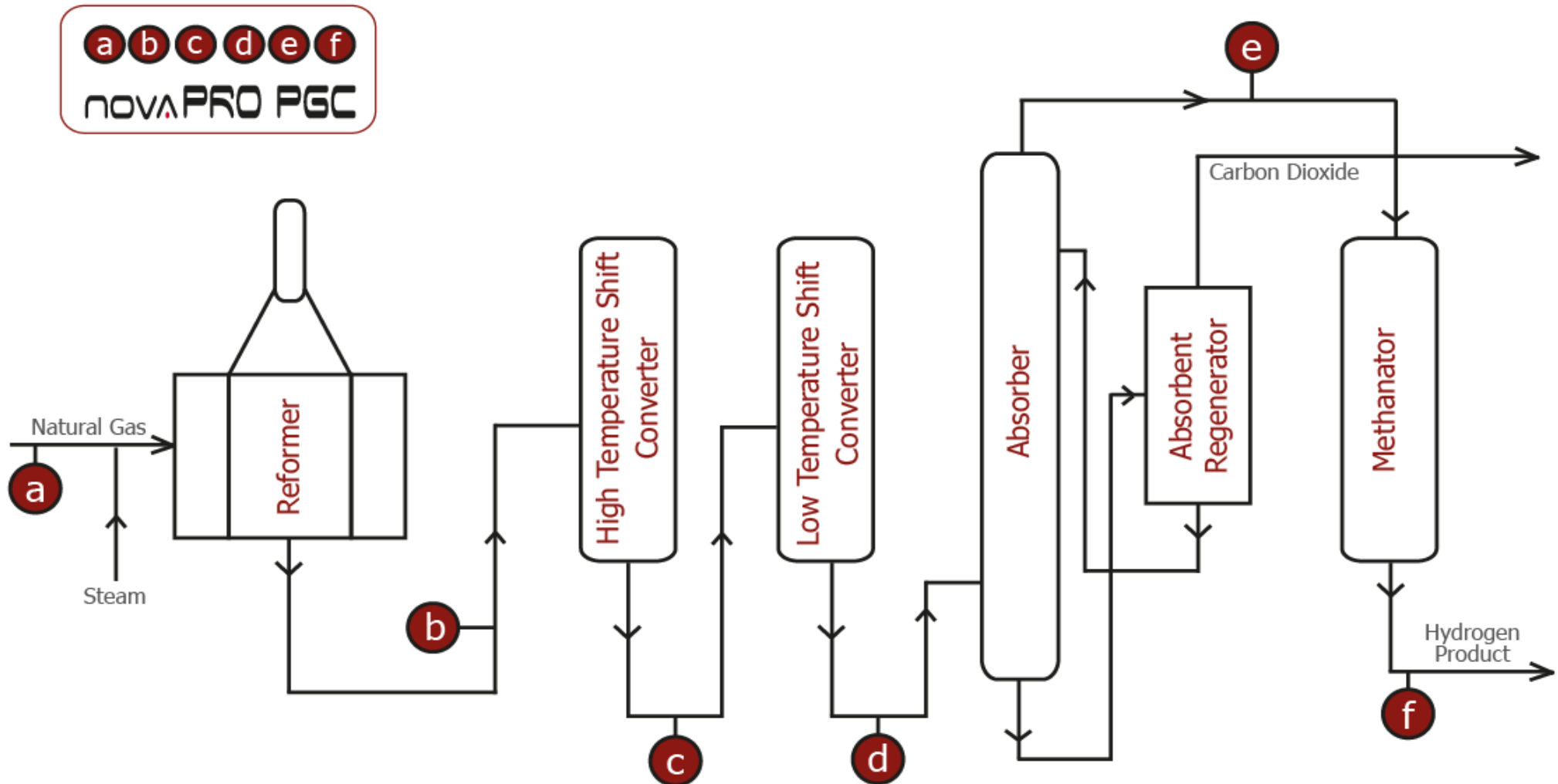
Analysis Time: < 7 mins
Carrier Gas: Hydrogen
Loop Size: 0.2µl
Columns: (1) 6 ft Hayesep DB
(2) 8ft Mol Sieve 5A
Detector: TCD

Detailed Analysis of CO, CH₄ & CO₂

Oxygen
Nitrogen
Methane
Carbon Monoxide

Analysis Time: < 3 mins
Carrier Gas: Hydrogen
Loop Size: 1cc
Methaniser:
Columns: 6 ft Hayesep DB
Detector: FID

Hydrogen Plant



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Application Note #10

On-Line PGC for Vapour Recovery

In the Refinery operation, the recovery of light gases and Hydrocarbons is essential. Nearly every refining and cracking process which produces gasoline fractions from heavier stocks produces substantial quantities of light Hydrocarbons from C1 through to the C4's. When segregated into various fractions for specific markets or for use in other refinery operations, they are most valuable.

They usually are:

❖ Hydrogen, Methane and Ethane For the refinery fuel gas system
❖ Propane For LPG sales
❖ Propane/Propylene For alkylation Feed
❖ Butane For LPG sales or gasoline blending
❖ Mixed Butanes For use in alkylation
❖ Mixed Butanes/Butylenes for alkylation feed
❖ C5+ For gasoline blending

It is uneconomical to incorporate light ends recovery into each process that generates them. The light ends from all the plant processes are sent to a Central Gas Processing plant for further concentration and fractionation.

A Vapour Recovery Unit may operate as a completely separate plant or may comprise a portion of one of the other major operating units such as the Fluid Catalytic Cracking Unit or the Crude Oil Distillation Unit. In these cases, gases from other processes can be diverted to these units for recovery. In some instances, two separate plants can be in operation for separate processing of saturate and unsaturated gas streams. The compositions of the streams will be different but the operations are similar in both cases.

Typical compositions can be seen in Tables 1 and 2.

A Recovery Unit will usually include an Absorber column, various fractionation columns with H₂S Removal and Treating Units. Schematic (1) shows a typical unit.

Liquid C3/C4 gas streams and Wet gases are fed to an Absorber and through contact with lean oil, the heavier Hydrocarbons are absorbed. A lean Oil consists of a gasoline fraction which can as light as C7's or as heavy as C10'.

It has been found that if lighter fractions are used there is an increased efficiency in the Absorber. It may require refrigeration for low temperature operation in the Absorber. All the Hydrogen, Methane and Inert gases are taken overhead. The C2's are split between the Overhead and the Bottoms product.

The De-Ethaniser removes the residual C2's in the Overhead which is then combined with the Absorber Overhead for use in the fuel gas system after treatment for H₂S removal.

C4's and lighter are then removed in the De-Butaniser, leaving only C5's and heavier in the lean oil. The De-Butaniser Overhead is processed by the liquid treaters for H₂S removal. H₂S is recovered and diverted to the Sulfur recovery plant for conversion to the Alkylation Sulfuric Acid or Elemental Sulphur.

The Gasoline splitter will remove the fraction boiling Pentanes and the molecular weight of the lean oil. Motor Oil is produced from the resulting light gasoline product. As the heavier ends build up in the lean oil, a portion is drawn off to Gasoline blending. If the recovery plant processes unsaturates, the De-Propaniser Overhead will be a Propane/Propylene mix and the Bottoms product will be a Butanes/Butylenes mix. Both fractions are used as Olefin feed to the Alkylation plant.

Process Gas Chromatographs are used extensively in Vapour Recovery Plants. Refer to Schematic (1) to see the various points.

Analysis Point (A)

This is the analysis of Ethane and Propane in the Absorber Bottoms, and is necessary for proper control of the Absorber. The lean oil circulation rate is adjusted to maintain the C2's and C3's in the bottom at a predetermined level or at some optimum ratio. Due to the large amount of lean oil in that stream, the Process Gas Chromatograph needs to use a Sample Valve which maintains the sample in the liquid under a pressure of several hundred psig.

Analysis Point (B)

This is in the De-Ethaniser Bottoms and similarly analyses Ethane and Propane. Heat input into the Re-Boiler is controlled to maintain the residual Ethane or the Ethane/Propane ratio at a predetermined level.

Analysis Point (C)

A Process Gas Chromatograph is used in the De-Ethaniser Overhead to analyse for C3's. C3's are more valuable as LPG or for Alkylation feed. The tower operation has to be trimmed to minimise the loss of these components in the Overhead product.

Analysis Point (D)

In the De-Butaniser, both the Overheads and Bottoms are analysed using gas chromatography in an effort to control the unit. It is necessary to minimise the C5 and heavier in the Overhead.

Analysis Point (E)

As the C5's & heavier in the Overhead of the De-Butaniser need to be minimised, the quality of the Bottoms needs to be controlled to minimise the C4 content.

Analysis Point (F)

In the De-Propaniser, the chromatographic analysis of the Overheads and Bottoms is necessary for product quality. The Overhead is analysed for C4 content either as iso-Butane specifically or as total C4's.

Analysis Point (G)

While the Overhead is analysed for C4, the Bottoms product should be maintained so that the C3 content is minimised.

Analysis Point (H)

The De-Isobutaniser must be analysed for optimum control of this unit. The tower operation is controlled to maintain the iso-Butane purity content of the Overhead at the optimum level.

Analysis Point (I)

The Bottoms product of n-Butane should also be analysed and the tower operation is trimmed to minimise the loss of iso-Butane in that stream. Efficiency of H₂S removal by the Amine liquid and gas treaters can be optimised by measuring the H₂S content of the feed streams. The H₂S content of the combined Absorber & De-Ethaniser Overhead Streams is analysed using a Gas Chromatograph. This measurement can be used to set the Amine circulation at the optimum rate. Similarly the H₂S content of the De-Butaniser Overhead at Analysis Point (D) is measured to assist in controlling the solution circulation rate to the liquid treater.

Analysis Point (J)

If the H₂S content of the H₂S rich stream to the Sulfur Recovery Plant is required for Accounting purposes, it may be analysed using a Gas Chromatograph at the Regenerator outlet. H₂S may be measured directly with an accuracy of $\pm 1\%$. If greater accuracy is required, the Hydrocarbon impurities may be determined individually, totalled, and the H₂S determined by the difference in results.

Table (1) Vapour Recovery Plant Typical System Composition Saturates Recovery									
Analysis Point	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)	(I)
	Absorber	De-Ethanizer		De-Butanizer		De-Propanizer		De-Isobutanizer	
	Bottoms	Bottoms	Overhead	Overhead	Bottoms	Overhead	Bottoms	Overhead	Bottoms
Methane	1	Trace	5						
Ethane	10*	2*	90	2		3			
Propane	10*	10*	5*	33		94	2*	5	
Iso-Butane	15	15	Trace	35	1*	3*	50	90	5*
N-Butane	10	10		25	2*	Trace	45	5*	90
Iso-Pentane	2	3		2*			2		5
Hydrogen Sulphide	1	1	1	2*					
C5+	51	60		1**	97		1		

*measured

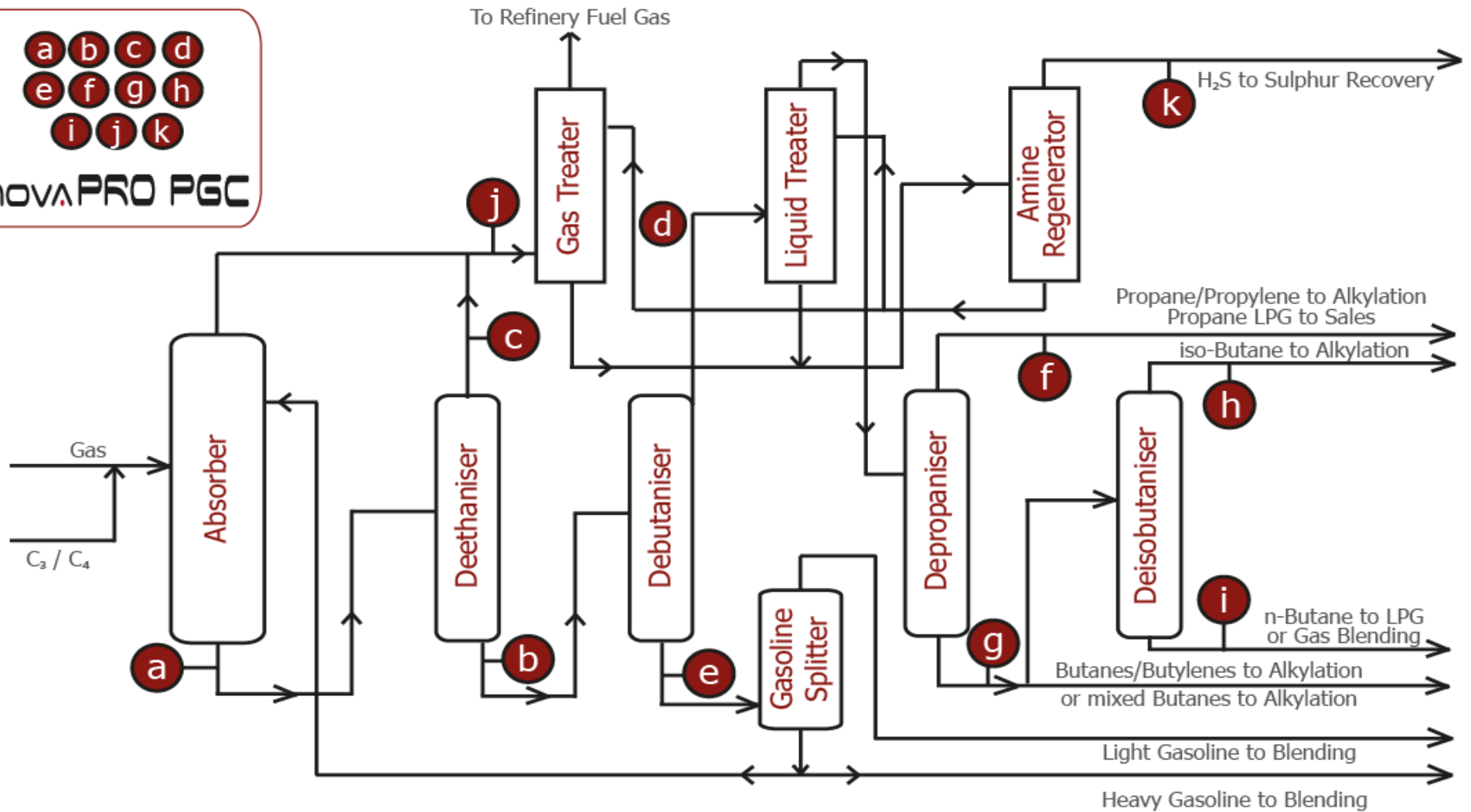
**optional

Table (2) Vapour Recovery Plant Typical System Composition UnSaturates Recovery									
Analysis Point	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(I)	(J)
	Absorber	De-Ethanizer		De-Butanizer		De-Propanizer		Gas Treater Feed	H ₂ S Products
	Bottoms	Bottoms	Overhead	Overhead	Bottoms	Overhead	Bottoms		
Hydrogen								15	
Methane	1	Trace	5					35	Trace
Ethane	5	1	45	Trace		Trace		20	<1
Ethylene	5	1	45	Trace		Trace		20	<1
Propane	6*	6*	3*	25		49	1*	3	<1
Propylene	4*	4*	2*	25		49	1*	2	<1
Iso-Butane	10	10	Trace	7	1*	1*	15	Trace	<1
N-Butane	5	5		8	1*	<1*	15		<1
Butylenes	10	10		30	2	<1	60		<1
Iso-Pentane	2	2		1*			2		Trace
Hydrogen Sulphide	1	1		2				5*	95*
C5+	60		2**	94			1		
Water									5

*measured

**optional

Vapour Recovery



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