GAS CHROMATOGRAPHIC DETERMINATION OF STYRENE IN COMPLEX PYROLYSIS GASOLINE

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ABSTRACT

Pyrolysis Gasoline (PYGAS) is produced by Yanpet in its Olefins Cracker plant as a byproduct during the cracking of ethane, propane and naphtha. The PYGAS product (C6-C8) rich in benzene content has it's usefulness in terms of sales to downstream aromatics processors. The byproduct, however, contains some styrene which is an unwanted monomer for downstream users as it polymerizes partially into polystyrene. Yanpet had a Double Hydrotreating Plant for PYGAS product purification called as DPG. An accurate styrene measurement is therefore needed to optimize the performance of DPG reactor for styrene elimination from the by product.

The paper presents a novel capillary gas chromatographic method developed at Sabic R&T, Riyadh to determine the styrene impurity in PYGAS product. Extensive experimentation was carried out for identifying suitable GC conditions to separate and quantify styrene from a complex organic mixture. The retention time of styrene varies as the concentration changes from ppm to percent, the conventional sample spiking techniques were found not reliable and therefore the sample was also investigated on GC/MS to identify the real styrene peak. The studies were conducted on standard samples prepared in varying concentrations up to percent level and analyzed on a multi level calibrated gas chromatograph to determine and demonstrate the detection linearity, limit of detection, accuracy and precision to validate the method for the intended application. The data of these studies shall be presented

Keywords: *Pyrolysis Gasoline, Olefins, Naphtha, PYGAS product, Gas Chromatography, GCMS, Aromatics, Styrene monomer, DPG Reactor, ppm*

الملخص

الغازولين (بيغاز) مواد ثانوية تتشكل خلال التفكيك الحراري لغاز الا يثان والبر وبان و النافثا في مصنع التحويل الحراري للاوليفينات لشركة ينبت . مواد البيغاز (س٦-س٨) غنية بمادة البنزين وهي مادة مفيدة وبالإمكان الاستفادة منها في صناعات العطريات. لكن هذه المواد تحتوي على مادة الستايرين وهذه المادة غير مرغوب فيها لأنها تتبلمر جزئيا وتشكل بوليستايرين . يوجد في شركة ينبت حاليا معمل مزدوج لمعالجة مواد البيغاز وتنقيتها. هذا المعمل يدعى د ب ج و لا يوجد فيه طريقة صحيحة لقياس مادة الستايرين لذلك يحتاج هذا المعمل إلى طريقة جيدة لتحسين فعالية المفاعل د ب ج و القضاء على مادة الستايرين في المنتجات الثانوية .

في هذه الورقة نقدم طريقة جديدة و مستحدثة بواسطة الغاز كرموتاغرفي الشعيري للكشف عن مادة كمية الستايرين في مواد البيغاز تم تطورها في معامل سابك للبحث والتطوير. خلال هذه الدراسة تجارب عديدة تم البحث فيها لإيجاد طرق لاختيار أفضل شروط مناسبة للج س لتحديد و فصل مادة الستايرين من عدد كبير من المواد العضوية المعقدة الأخرى .

لقد وجد أن الوقت اللازم لمادة الستايرين لتمر خلال اقنية الجي سي الشعيرية كان قد تغيّر بتغير تركيز مادة الستايرين من جزء بالمليون إلى جزء بالمائة وكذلك وجد أن الطريقة المعروفة بالحقن الاستدلالي للعينة لم تكن صالحة فالعينة قد فحصت على جهاز الج سي\ام اس للكشف عن آثار مادة الستايرين . هذه الدراسة كانت قد نفذت باستعمال عدة عينات معروفة التركيز حضرت بكميات مختلفة و منها وصل إلى التركيز المئوي وفحصت جميعا على جهاز الغاز كروموتاغرفي متعدد المستويات لتحديد علاقة التناسب والدقة والصحة لوضع الأسلوب الجيد للتنفيذ.

1. INTRODUCTION

PYGAS is produced at Yanpet in its olefins Cracker plant as a byproduct of the cracking of ethane, propane and naphtha. The PYGAS product (C6-C8) rich in benzene content has it's usefulness in terms of sales to downstream Aromatics processors. The byproduct contains some styrene and this is an unwanted monomer for downstream users because it adds no value in their processes, and can partially polymerize to polystyrene. Yanpet had a Double Hydrotreating Plant for PYGAS product purification called as DPG. In the first stage reactor, pyrolysis gasoline is hydrogenating at low temperature in liquid phase, where diolefin, styrene, acetylene and other unstable compounds are selectively hydrotreated on Palladium catalyst (G-68C-1 catalyst) into, olefins, paraffins, and aromatis. The styrene content of the first stage products should not be allowed to exceed 0.3 wt%. These specs. determine the level of fouling precursors for the second stage. Exceeding the specs. can lead to fouling in the second stage reactor. The conditions of DPG Reactor govern the purification process including the elimination of styrene from the raw PYGAS. The elimination of styrene from the raw PYGAS largely depends on the following variables,

- First stage temperature:
- First stage pressure
- First stage excess hydrogen
- First stage liquid recycle

In the 2nd stage reactor, the olefin, sulfur compounds, styrene and residual diolefins are completely hydrogenated. Therefore a fast analytical method to quantify styrene is required to monitor and optimize the different stages of DPG plant reactor for the complete elimination of styrene from the by-product.

The volatile liquid products and byproducts formed during cracking of petrochemical feed stocks present a myriad of challenges to the gas chromatographer. Not the least of these is the selection of proper method of analysis. By this, we mean finding the method that gives the

required answers in a speedy, economical way. This, in turn implies the necessity of the analyst's understanding of his customer needs as well as knowledge of the analytical tools available. In fact, it is a proven experience that more analytical failures occur because of lack of communication between the analyst and his customer than because of lack of skill or tools on the part of analyst. Chromatography can provide much of the information and knowledge required to convert byproduct streams into profitable products.

The hydrocarbon mixtures considered here are amenable to two different concepts of chromatographic analysis. These are high-resolution and low-resolution methods. The former always involve capillary column gas chromatographic techniques, and the latter involve packed column methods. Use of capillary columns in petroleum industries is routine for resolving the separation problems of complex organic mixtures and the selection of liquid phase has the greatest influence on the elution order of the components from a column [Whittemore I. M., 1979]. Gas Chromatography is currently the main technique for the determination of the composition of complex hydrocarbon mixtures. GC equipped with Flame Ionization Detector (FID) is widely used to detect hydrocarbons in the range from ppm to percent levels with fast speed, high sensitivity and reproducibility of the results [Pimental J. C. et al., 1987], [Muir, A. L. ,1997] & [Proceedings,1998].

This paper discusses the development of a fast and efficient capillary GC method for the determination of styrene in the PYGAS by-product streams. The method was developed and standardized on the request of Yanpet plant. Data for precision, accuracy, and statistical process control chart are presented to demonstrate method validation. Preliminary analysis by GC-MS for the identification of the components is also included.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

Ethyl acetate (purity – 99.0 +%) from BDH was used as solvent and styrene (purity – 99.0 +% minimum) from Aldrich was used for the preparation of standard calibration blend. Toluene and benzene (purity > 99.5% each) from Aldrich were used during method validation.

2.2. Preparation of Calibration Standards

Styrene stock solution (1250 ppm wt/wt approx.) in ethyl acetate was prepared by weighing around 0.0312g of styrene in a 30 mL glass vial on a Mettler balance and adding the solvent to make it 25.0 g. The solution was shaken on a mechanical stirrer for 15 minutes to homogenize it. Styrene standards in 8 levels eg., 3.0, 13.0, 26.0,46.0, 60.0, 94.0, 180.0 and 550.0 ppm were prepared from this stock solution for GC calibration. Styrene 0.8 ppm standard was prepared by mixing 1.0g of 3.0 ppm above standard with 3.0g of ethyl acetate. This standard was shaken as above and injected to the GC for the determination of detection limit of the

method. Similarly 8 levels of calibration standards with styrene in 3 ppm to 7.5 % range were also prepared.

2.3. Instrumentation

Standards and PYGAS samples were analyzed on HP 6890 GC using auto sampler. The GC was programmed to the following conditions,

2.4. GC Conditions

Column – SPB tm-5, 30m x 0.25mm x 0.25um from Supelco, cat # 24034

Oven Temperature profile - 50°C for 2.0 min, ramp rate-1 5°C, final temperature-1 120°C, ramp rate-2 40°C, final temperature-2 240 °C for 5 mins.

Carrier gas – He, flow – 1.2 mL /min, split ratio – 100:1

Inlet temperature - 230°C and FID temperature - 250°C, Sample injection volume – 1.0ul

2.5. GC-MS Conditions

GC-MS:	Shimadzu QP 5050A
Injector:	Split at 230ºC
Injection volume:	0.5ul
Column:	SPB tm-5, 30m x 0.25mm x 0.25um
Temperature Program:	50ºC – 2 min / 5ºC / 120 ºC-0.0 min./40ºC/240ºC – 5 mins.
Carrier Gas:	Helium at 0.5 mL /min
MS Conditions:	Full Scan (m/z 35 – 450, sampling rate 0.5 sec)

Each standard was analyzed in 3 replicates for GC calibration. The samples were analyzed as and when received from Yanpet. One level of the standards was also analyzed in 25 replicates for determining the precision and accuracy of the method. Data for SPC chart were generated with the help of one of the Pygas sample being analyzed in 25 replicates over a period of one month.

Method validation was done by preparing a solution of benzene and toluene according to their concentrations in the Pygas sample with zero and 100 ppm styrene as reference matrix and mixing in 1: 1 ratio with the sample. These samples were also analyzed in 3 replicates each.

3. RESULTS AND DISCUSSION

Gas chromatogram of the Pygas sample is shown in figure-1. Chromatogram revealed a complex components profile and identification of styrene peak was confusing due to close elution of other components there. GC-MS analysis with slightly changed conditions helped in the identification of each resolved peak and thus removed the doubt of styrene identification. Moreover, retention time of a component during GC analysis shifts if its concentration varies

from ppm to % level. Sometimes the raw PYGAS contains styrene to 7.0%. During the GC-MS analysis injection volume was reduced to 0.5ul and helium flow to 0.5ml/min to avoid mass detector saturation and close elution of the components. High vacuum of GC-MS compensates the flow reduction. The components identified in the Pygas product sample by GC/MS are reported in table-1.

Table 1: GC-MS components profile of PYGAS Product sample

Sr.#	Components	Sr.#	Components
1	Cyclopentane	12	Toluene
2	2-Methyl pentane	13	n-Octane
3	3-Methyl pentane	14	Ethyl cyclohexane
4	n-Hexane	15	Cyclooctane
5	Methyl cyclopentane	16	Ethyl benzene
6	Cyclohexane	17	p- & m- Xylenes
7	Benzene	18	1,3-Dimethyl cyclopentane
8	2-Methyl hexane	19	Bicycloheptane
9	n-Heptane	20	Bicyclo octane
10	Ethyl cyclopentane	21	Styrene
11	Methyl cyclohexane	22	o-Xylene

GC-MS analysis also revealed the close elution of styrene and o-xylene peak in the chromatogram. The spiking of styrene with the addition of pure component could have caused confusion in a simple GC run and hence the GC-MS analysis removed this doubt.

GC calibration with multiple levels of styrene external standards in 3.0 – 550 ppm wt/wt (figure-2) range gave a linear curve with regression factor – 0.99993. Similar curve was also obtained when the GC was calibrated in 3.0 – 1250 ppm range and thus explains the application of this method in a broad concentration range of styrene to be determined in the sample. Same linearity was found even to 7.5 % concentration of styrene. The detection limit of the method was also determined and found to be 0.8 ppm (figure-3). The data was generated after rejecting signal to noise ratio of 3:1.

Test precision in terms of repeatability was determined +- 1.052 based on 95% (2 σ) confidence level with RSD – 1.77 % for 25 replicate analysis of 26.0 ppm standard. Moreover, Statistical Process control (SPC) chart (figure-4) with 25 replicates each of the standard and the PYGAS sample respectively fulfilled the quality of the results with no significant variation in the method. Generally 60 data are required for SPC chart generation which was not possible in our lab due to so many other work loads. In case the SPC chart does not show any uncertainty of the process, 25 replicate readings are also reported to fulfill statistical requirements [Montgomery D.C., 1996].

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Method validation data are represented in figure-5. Styrene contents of 13.5, 27.0 and 65.0 ppm were determined by the addition of PYGAS product sample with reference matrices mentioned in the experimental section. The reduction to 13.5 ppm from 27.0 ppm and increment to 65 ppm concentrations justify the validity of our data. Other suitable labs were not found to analyze PYGAS samples for method validation due to no availability of the procedure there.

Styrene concentration determined by this method in some of the raw PYGAS and product samples are reported in table-2 and figures-6.

Table 2: Amount of Styrene determined in PYGAS samples by GC:

Sr.#	Sample I. D.	Analysis #1 Conc. ppmw	Analysis #2 Conc. ppmw	Average Conc. ppmw
1	Raw PYGAS	1227.0	1236.0	1231.5
2	First Stage Outlet	525.5	516.9	521.2
3	First Stage Outlet	501.6	496.2	498.9
4	First Stage Outlet	533.7	531.2	532.5
5	Second Stage Outlet	50.5	51.4	50.9
6	Second Stage Outlet	41.4	47.3	44.3
7	Second Stage Outlet	42.7	43.2	43.0
8	Second Stage Outlet	46.0	39.9	43.0
9	PYGAS product	26.0	28.0	27.0
10	PYGAS product	22.5	23.5	23.0
11	PYGAS product	18.0	16.0	17.0

The above data helped Yanpet process engineers during the DPG reactor tuning and achieved a reduction of styrene concentration from 1231 ppm to 17 ppm in the PYGAS samples.

4. YANPET PROFITABILITY IMPROVEMENT

By reducing the styrene level in the PYGAS product YANPET gain extra netback by 25 USD/MT, here are Yanpet's profitability improvement:

- Average daily production is **435** MT/D
- On stream Factor (plan) = 90%
- Average annual production is **140940** MT/D
- Achieving an extra 25 USD/MT netback add **3523500** USD (or 13,213,125 SR) per Year to Yanpet profitability.

5. CONCLUSION

An External Standard (ESTD) method was developed on a capillary gas chromatograph, after extensive experimentation, that provide highly sensitive, accurate and reproducible determination of styrene in Pygas samples. The retention time of styrene varies as the concentration changes from ppm to percent, the conventional sample spiking techniques were found not reliable. GC-MS analysis was found useful to identify styrene with its molecular ion peak and peculiar ion fragmentation pattern and thus removed the doubt of any overlapping peak if any. An over view of the presented data also demonstrate the validity of the method. The accurate styrene data helped the plant to fine tune the DPG reactor for efficient performance that ultimately resulted in to a gross profit of over 13 million Saudi Riyals.

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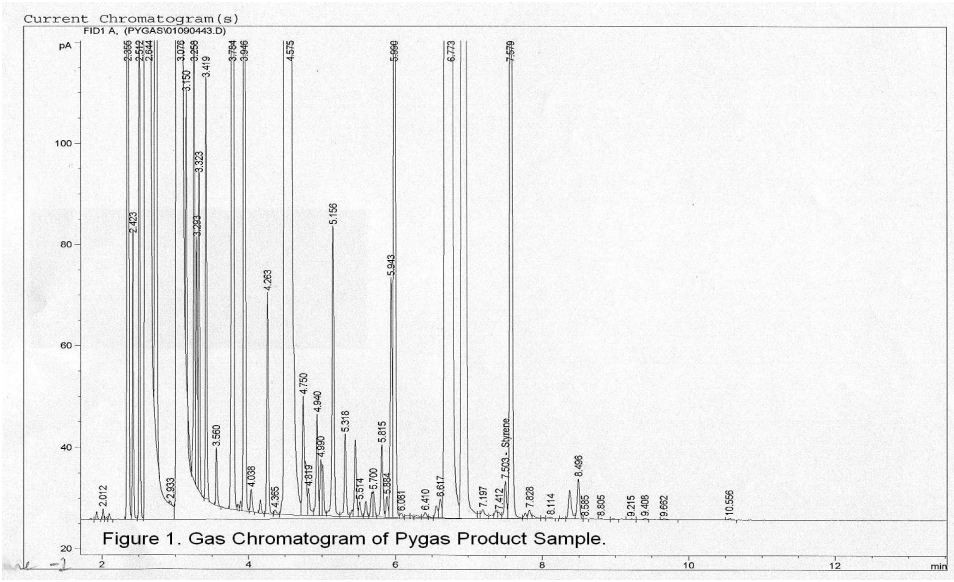

Figure 1. Gas Chromatogram of Pygas Product Sample.

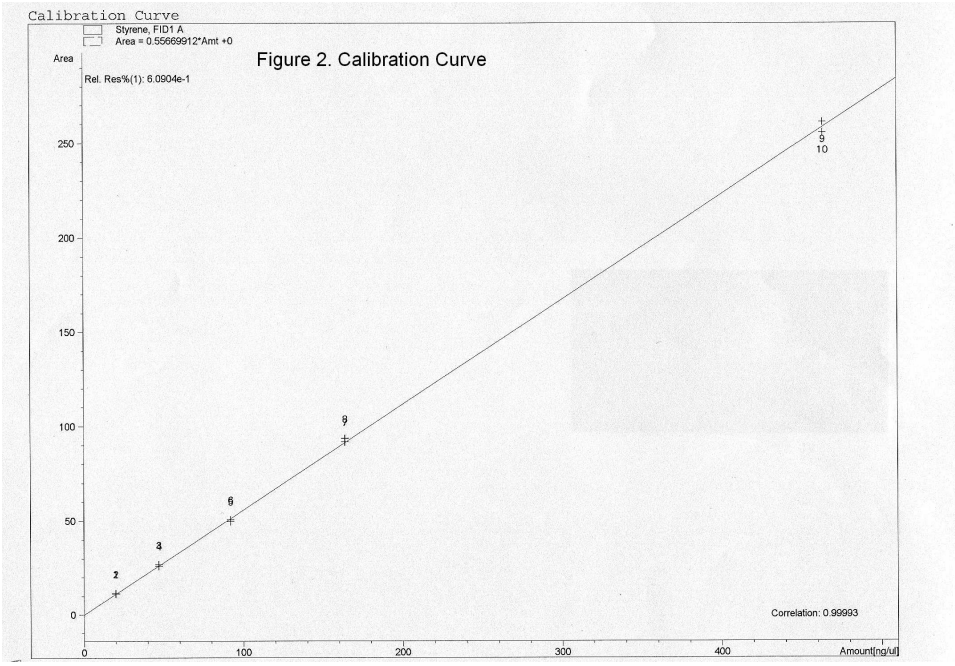

Figure 2. Calibration Curve

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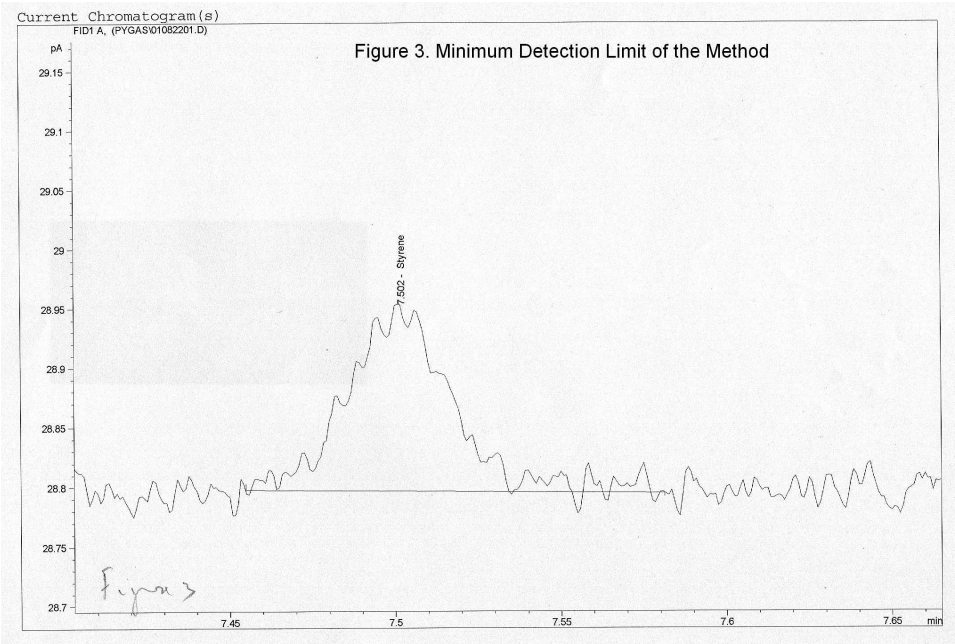

Figure 3. Minimum Detection Limit of the Method

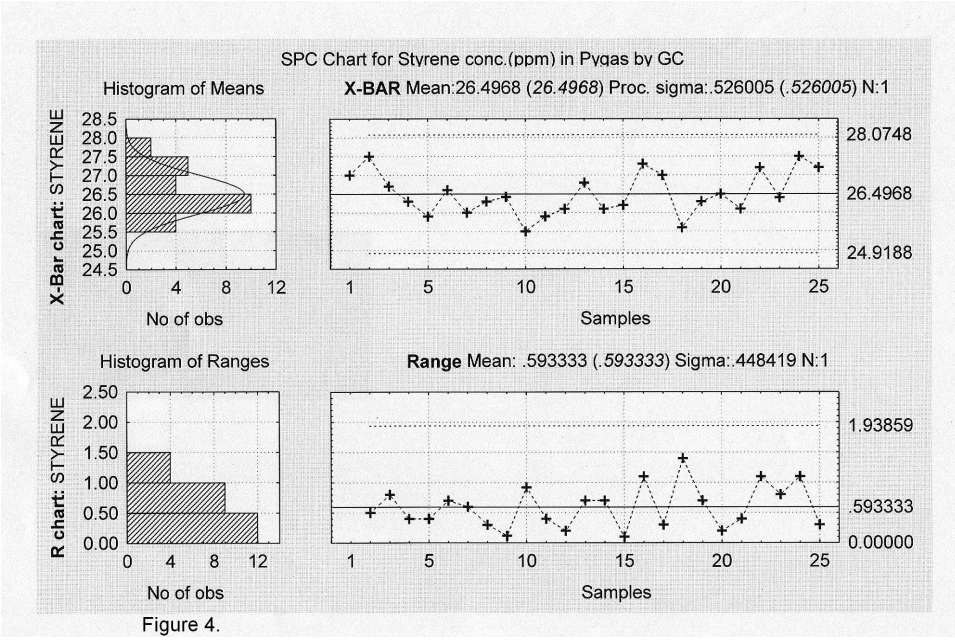

Figure 4.

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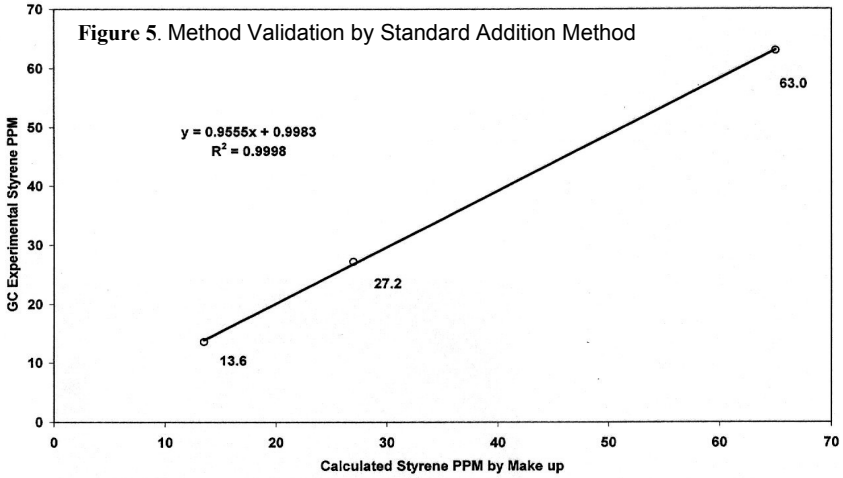

Figure 5. Method Validation by Standard Addition Method

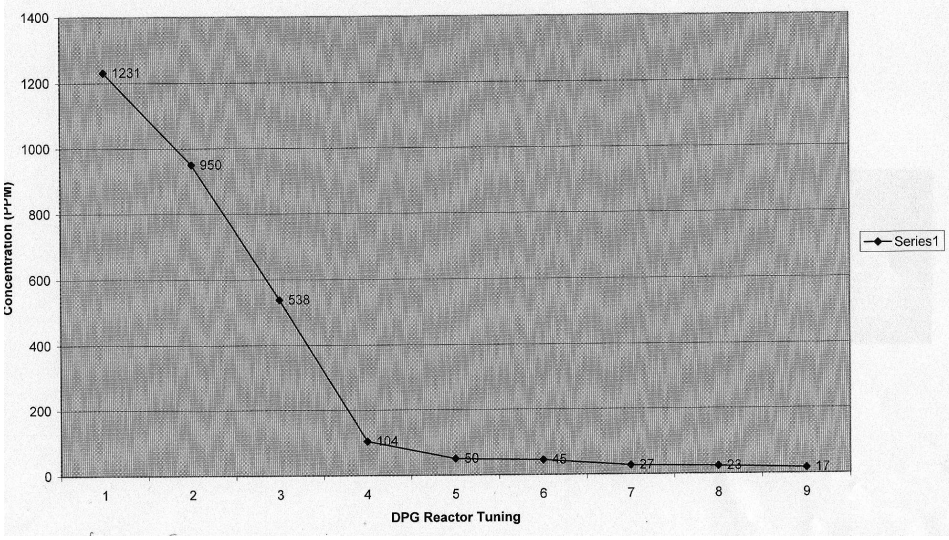

Figure 6. **Styrene Reduction in Pygas**

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