Well Stimulation Using Scrap Tires

Final Report

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Abstract

The following is the final report summarizing the results of the testing performed under grant 41880-RJLG-DOE-2098.

Three wells were located for field testing. One gas well is near Chautauqua, New York and two oil wells are near Yawkey, West Virginia. Samples of paraffin and oil from each of the sites have been characterized and evaluated for dissolution/suspension in DESolv™ at various temperatures. Based on these laboratory tests it was determined that unmodified DESolv™ would dissolve all three paraffins at the temperatures anticipated in the wells and that it will remain dissolved at ambient outdoor temperatures.

The wells in West Virginia were treated on 6/14/2011 and 6/15/2011, respectively, and allowed to soak undisturbed for several days. Preliminary data on these wells showed that the solvent penetrated the formations. After restarting, the pumping showed an increase in oil production for several days followed by a progressive decrease to pre-treatment levels. Indications from this well and experience from other wells suggests that a second and, maybe a third treatment could have potentially increase the period of increased production. Also, an acid treatment might have improved the effectiveness of the treatments. However, this was not within the scope of this study. The well in New York was treated on 7/8/2011. This well was much more problematic and could not be pressurized. Due to the open structure of the formation, the treatment chemicals enter the formation quickly and pumped out almost completely with the initial pump-out. This well produces oil in addition to gas. Treatment and production data from this well showed a short-lived effect of the treatment scheme. The large amount of brine produced by this well posed issues that would require a more aggressive approach to ensure the chemical treatment penetrates the formation and interacts with freshly formed surfaces.

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1.0 Introduction

Delta-Energy and RJ Lee Group have developed a catalyzed process for producing value added products from scrap tire materials. The research supported by this grant focused on application of the tire derived liquid product from this process, DESolv™1. Compared to commonly used solvents, previous evaluations have demonstrated DESolv™'s superior solvent properties for dissolving tars and paraffins. Delta-Energy has demonstrated that this solvent can enhance oil production in stripper wells having asphaltinic deposits that have obstructed oil and gas production. The purpose of this study was to test the effectiveness of DESolv™ in enhancing oil and gas production in wells that have been obstructed by paraffinic deposits.

The study was broken into two phases, 1.) laboratory testing and 2.) well field testing.

2.0 Experimental

Experimental/Laboratory Testing

The purpose of this part of the study was to evaluate mixed solvent systems based on DESolv™ that would have optimum solvent properties to dissolve and/or suspend the paraffinic solids found in Pennsylvania/New York/West Virginia crudes.

The solubility of crude oil solids are known to be highly dependent on the balance between aromatic and aliphatic components in the liquid matrix (crude oil). In addition, the presence of polar compounds in crude oil and/or the presence of water, especially brines, pose other issues that can require the use of dispersants and other surface active additives.

The scheme below was used to as a guide to tailor DESolv™ for optimum application in the test wells. Several solvent systems were evaluated in the laboratory based on these theoretical considerations. These properties have to be taken into consideration to optimize the treatment solvent.

[1] DESolv is a trademark of Delta-Energy, LLC.

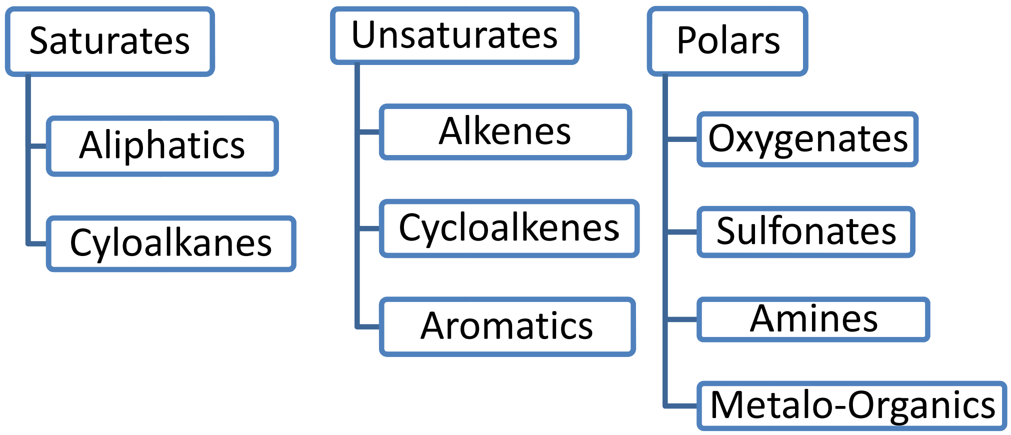

Figure 1. Outline of Solvent Properties.

The following solvent systems were prepared and tested by vortexing with approximately one gram of well solids from the test wells in 40 ml vials. Below are the test solvent systems that were evaluated with their solvent component distribution described in Figure 1.

DESolv™	▪ 25-32% linear and branched alkanes, also known as paraffins ▪ 20-30% cycloalkanes (also called cycloparaffins or naphthenes) ▪ 38-44% aromatic hydrocarbons ▪ 1-3% polar organics
Stoddard Solvent (white spirits)	▪ 30-50% linear and branched alkanes, also known as paraffins ▪ 30-40% cycloalkanes (also called cycloparaffins or naphthenes) ▪ 10-20% aromatic hydrocarbons
Mesitylene (trimethylbenzene)	▪ Highly non-polar aromatic
Limonene (methyl-ethylethenyl-cyclohexene)	▪ Non-polar solvent
NuGreen Solvent System	▪ NuGreen is a company that produces tailored solvents for down well application that are based on modifications of DESolve™. A general solvent that is believed to work on deposits and crude oils similar to those of interest here.

Shaker Tests at Elevated Temperature

Preliminary laboratory tests were done to investigate dissolution/suspension of well deposit material at various temperatures by shaking. In these tests a known amount of deposit material was placed in a vial with solvent. During shaking the material was warmed in a heating block to the test temperature (Figure 2.). Vials were examined over time for up to 72 hours. Records of the appearance of solids of the solids material were recorded. Based on these experiments it was found that DESolv™ at 60°C dissolved solids from wells in both locations and that the solids would remain dissolved even when the solvent was re-equilibrated to room temperature.

Figure 2. Apparatus for Shaker Tests

Mechanical Testing

The purpose of this part of the study was to test a variety of solvents developed above with solids from the test wells under conditions that simulate the mechanical and physical condition expected to be encountered in the wells.

Typical temperatures at the bottom of the test wells are expected to be on the order of 60 °C or above. Solvents would be typically pumped using a piston type pump with a low linear flow across the deposit material. We have setup the system described below and shown in Figure 3.

Miniature Piston Pump

A miniature piston pump as shown in the figure below was used to simulate the well pump. The solvent and deposit material were added to a sealed vessel with a circulating pump and a controlled heat source (Figure 3).

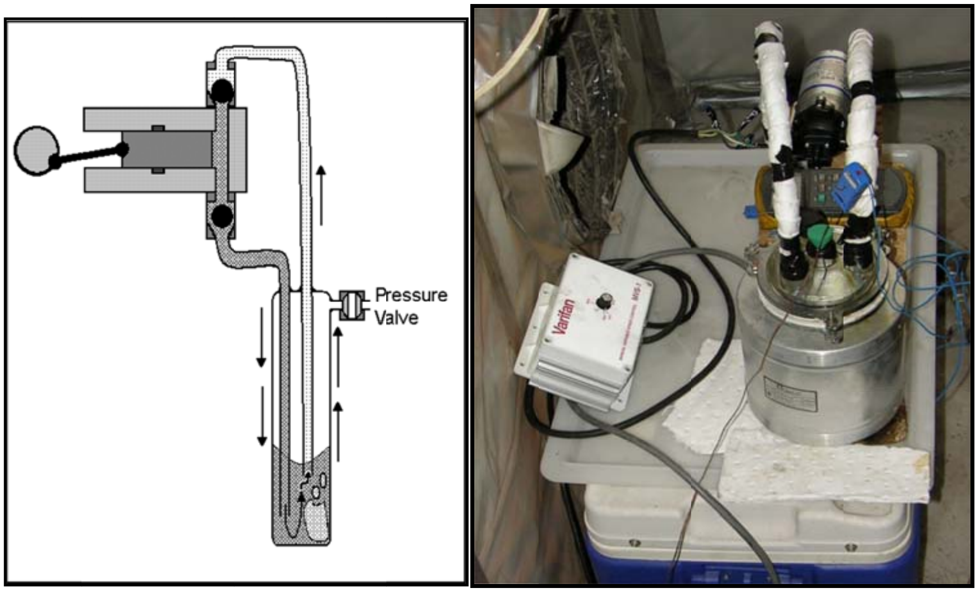

Figure 3. Mechanical Pumped System

Summary of Laboratory Testing

The deposit material was exposed to each test solvent under conditions of temperature and flow comparable to the conditions in the test wells. The samples were examined periodically to determine the time necessary to make the solids “pumpable” (either dissolved or dispersed and suspended). The most effective solvent for each test well deposit/crude oil combination was identified.

Experimental/Field Testing

General Protocol for Down Well Treating with DESolv™

Each well has its own characteristics; therefore samples of oil or deposit material were obtained from each well for laboratory analyses. The results of the analyses demonstrated that DESolv™ did not need to be augmented provided the well temperatures exceeded around 60ºC during the treatments. The well operators confirmed that this was the case for the three wells evaluated.

The following information was collected for each well:

- Well Depth
- Casing size
- Well pressures
- Liquid height
- Formation information
- Flow rates
- Perforations information

Well Treatment Solution Application

- Approximately 100 to 500 gallons of a treatment solution was used, depending on well and solvent characteristics.

- The treatment formulation was determined based on the results of the laboratory tests.
- The actual amount of treatment solvent and conditions were adjusted based on the well information and laboratory tests.

Review well maintenance

- Prior to treatment the well conditions were observed.
- Any suspect well equipment (e.g. pump) were repair or replace

The well treatment was schedule with the operators

Chemical treatment was pumped down the annulus.

- Wells were pumped off to decrease fluid levels in annular casings to the lowest level possible (note that in the NY well, which is a combined gas/oil well, there was too much fluid, mostly brine, to allow this)
- The annulus casings were pre-wetted (with 100 – 200 gallons of a DESolv/crude oil mixture)
- Well treatment chemicals were pumped down the annulus
- The well was allowed to soak for at least 30 minutes then the pump jack was started and run for 10 minutes allowing the chemical to sit inside tubing
- The well was closed in and nitrogen was utilized to pressurize the well, forcing the chemical treatment into well formation. For this the bottom hole pressure needed to be exceeded. (note that in the NY well, this was not possible)
- If needed, the well treatment (soak) was maintained under nitrogen pressure for 48 to 72 hours.
- After the soak time the well was circulated for 24 to 48 hours
- After treatment the well was placed back into production

Production Expectations Based on Experience with Asphaltinic Wells

- Increase well pressure
- Immediate increase in production output
- Level off of production over a period of time
- Higher sustainable production output after chemical treatment
- Monitor production output to determine when to retreat the well.

Down Well Treating of West Virginia Wells with DESolv™

- Pre-examination of the West Virginia wells was done in February 2011.
- Two West Virginia Oil wells were selected for testing
- Based upon the initial trip, communication with the well owners and staff data, and laboratory testing of well samples in the RJ Lee Group laboratory, a determination was made to move forward with the down well testing in these wells.
- A second trip was made in June 2011 to observe and guide the treatment. RJ Lee Group supervised the down well testing of DESolv™ in a number of asphaltinic wells at various locations in the US.
- One well was treated and oil and DESolv™ samples were collected and shipped to the laboratory. The photographed process can be seen in Figure 4.

- The second well was done the following week in June 2011 while RJ Lee Group was not in attendance.
- Liquid levels in the well were determined by soundings before and after – liquid heights and pressure were based on material density and height
- Pre- and Post-treatment samples were sent to the laboratory.

Treatment sequence of WV wells - East Resources Harris Oil treated 2 wells (see Figure 4).

- Rakerd well
- Oil was pumped down
- Tanker containing DESolv™ was connected to piping
- Sounding depth measurement taken
- DESolv™ was pumped into well
- DESolv™ was sampled
- Pressure gauges were used to monitor uptake
- Gauge volume measured DESolv™ pumped
- Tank was checked to confirm level
- Oil was collected from tank to top off DESolv to pressurize
- Total added ~500 gal DESolv™ plus 358 gal crude on top
- Sounding for depth measurement was taken once more
- Atmosphere safety checks were performed for toxic or explosive gas levels
- Pumping and sampling crude
- Total pumped 568 gal DESolv™ +~289 crude (~35API)
- Circulation for 10 min to clean pump and tubing
- Well was left idle for 6 days to allow dissolution and penetration
- It was circulated for 2 days
- Based on pressure, half of DESolv™ went into formation (net hydrostatic pressure 696 psi)
- Hilbert well was treated with a similar treatment and took all of the DESolv™ into the formation

Lown Aten (NY)

- RJ Lee Group employee visited site
- Examined initial well and it was not ready for testing
- Well was just producing a small amount of gas and no oil
- New tubing and pump were install.
- NY treated with 700 psi natural gas
- DESolv™ was pumped into the well annulus followed by crude oil from the tank
- The well was allowed to soak
- After the soak period the well was put back into production.

Figure 4. Showing Treatment of Rakerd Well Treatment Sequence.

a. Rakerd Well; b. Tanker with DESolv™; c. Depth Sounding ; d. Pumping Down; e. Sampling DESolv™; f. Monitoring Well Pressure; g. Checking Tanker Level; h. Hooking up to Tank Oil; i. Depth Sounding; j. Safety Monitoring; k. Sampling; l. Volume Monitoring.

Samples Received

Table 1. Samples Received from the Field.

RJLG #	Sample ID	Description	Received From
3076222	030111-1 (asphaltene control)	Well Deposit	Colip, Iowa
3076223	030111-2 (asphaltene control)	Well Deposit	Colip, Iowa
3076550	Paraffin Wax	Lown-Aten Unit #1	Lenape Resources, Inc, NY
3076551	Crude Oil	Lown-Aten	Lenape Resources, Inc, NY
3076552	Brine	Lown-Aten	Lenape Resources, Inc, NY
3076553	Sludge (well bottom)	Rakerd	East Resources, Yawkey, WV
3076554	Paraffin Wax	Rakerd	East Resources, Yawkey, WV

- Samples 3075869 and 3075871 are control samples and solvent, respectively.
- Sample 3075870 is a test paraffin from a local gas well.
- Samples 3076222 and 3076223 are heavy crude oil containing asphaltenes from an oil well in Iowa operated by Lynn Colip. It is being used as a control sample.
- Samples 3076550, 3076551, and 3076552 are from oil gas wells operated by John Holko of Lenape Resources. Sample 3076550 is a paraffin wax to be treated.
- Samples 3076553 and 3076554 are from an oil East Resources. Sample 3076554 is a wax that was scraped from bars and is contaminated with soil, rust and other contaminants. Sample 3076553 is from the taken bottoms and contains crude oil and solids (probably brine and paraffins). Mike Wilmoth is trying to get clean paraffin and crude from them.

3.0 Results and Discussion

Laboratory Testing

Although various modified DESolv™ solutions were tested the laboratory testing demonstrated that the paraffins from all both well sites would be dissolved and remain in solution by unmodified DESolv™ under the conditions observed in the wells. Based on viscosity of the post treatment samples no issues were anticipated in being able to pump the resulting crude oils. The results of the laboratory tests are summarized in the following tables.

Field Testing

Post-treatment tests on the crude oil showed a significant decrease in the C5 insolubles as well as fewer visible solids. The GC analyses showed no indications of detrimental changes to the crude oil produced. 6PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine), an antiozonant in DESolv™ was used as a marker to monitor for the presence of DESolv™ in the post-treated crude oil from the wells. Based on this monitoring there was little to no DESolv™ remaining in the post-treated Lown-Aten well. The Rakerd and Hilbert wells both had on the order of 10% DESolv™ remaining in the after treatment sample. ICP analyses for metals (see Table 2) only detected very low levels of calcium and on the order of 0.2% sulfur. The sulfur in the post-treatment samples was increased by about 0.06%, which is consistent with approximately 10% residual DESolv™.

The wells, Rakard and Hilbert, were treated on 6/14/2011 and 6/15/2011, respectively. They were first pumped down with crude oil and approximately 9 drums of treatment was pumped into the wells. This was followed by crude oil to push the treatment into the deposit. The oil was then circulated for 10 min to clean pump and tubing, the wells were shut-in for 6 days, followed by 2 days circulation. After restating production the level rose to approximately double the pre-shut-in levels and and dropped after a month.

A brief description of the Lenape Resources Lown Aten LRC #317 well in Ellery Township Chautauqua County NY and treatment is described below.

Other than natural gas to the homeowner, this well had been shut in for approximately 36 months prior to treatment. The well is located in a faulted interval of the Onondaga Limestone which produces oil/gas/water. It was shut in due to high water cut thought to have been caused by paraffin precipitation on the perforations and formation.

The well was treated on 7/8/2011 with 5 drums of treatment. We were unable to pump the well off due to high fluid levels and treated from the surface. After a 7 day shut-in, the well was placed back into production. Prior to treatment and during the first 5 days of production, oil production average approximately 4 bpd, during the next 2 months, the average dropped to about 2 bpd and is currently producing about 1 bpd. According to the well operator this response is typical of this well and seems to indicate that the treatment may have improved initial flow, but was unable to improve overall oil to water ratio.

Possible issues may have resulted from the flow regime of this well being a high permeability fault versus standard porous sandstones. It was also apparent that the chemical retention time in this environment was also short leading us to believe the chemical was unable to attach itself to the formation for longer term enhancement.

As expected for this well, production data showed initial increase in oil production but, levels rapidly fell to pre-shutdown levels and below. It is likely that DESolv™ played a roll in reestablishing flow in this well but, since the well was previously shut down, it is difficult tell how much effect it had from the available data.

In retrospect the acid treatment prior to this treatment regime could have provided fresh surfaces for DESolv™ to absorb to, making it more effective. We would need to pump down the well as much as possible to ensure contact of the DESolv™ with the formation.

Both the Rakard and Hilbert wells showed an immediate increase in oil production after treatment which decreased in a short time post-treatment (see Figure 8). Our previous experience with wells that perform this way is that further dosing would extend the increased production period. With these well, acid treatment might have proven valuable in enhancing the effectiveness of DESolv™.

Table 2. Laboratory Data Collected for Well Samples.

State (well #) Well Name Pre- or Post- Treatment or Solids RJ Lee Group Sample ID	NY (1) Lown-Aten Pre 3076551	NY (1) Lown-Aten Post 3078510	NY (1) Lown-Aten Solids 3076550	Wva (1) Rakerd Pre 3076553 3078056	Wva (1) Rakerd Post 3079267	Wva (1) Rakerd Solids 3076554	Wva (2) Hilbert Pre 3076553	Wva (2) Hilbert Post 3079265	Wva (2) Hilbert Solids 3076554
Flash point	0°C	0°C	N/A	15°C	-5°C	N/A	15°C	<-5°C	N/A
Pour and/or cloud points	-27°C	-36°C	45°C	-18°C	-30°C	78°C	-18°C	-30°C	78°C
Kinematic viscosity at 40°C and 100°C	N/A	4.916- 1.87	N/A	N/A	4.178- 1.88	N/A	N/A	3.729- 1.7	N/A
viscosity index	N/A	~295	N/A	N/A	534		N/A	798	N/A
GC/MS %DESolv™ (see related Graphs)	0.0%	0.0%	N/A	0.0%	7.0%	N/A	0.0%	13.2%	N/A
ICP scan (Wt%) **Calcium** Iron Potassium Sodium **Sulfur** Vanadium	N/A	**0.000943** < 0.00124 < 0.00124 < 0.00124 **0.0943** < 0.000248	N/A	**0.000968** < 0.00118 < 0.00118 < 0.00118 **0.112** < 0.000236	**0.000857** < 0.00125 < 0.00125 < 0.00125 **0.159** < 0.000250	N/A	**0.000968** < 0.00118 < 0.00118 < 0.00118 **0.112** < 0.000236	**0.00072** < 0.00111 < 0.00111 < 0.00111 **0.202** < 0.000222	N/A
CHONS (LECO) Comments	Aliph:Arom 73%:27%	N/A	Median Wax C35H70	Aliph:Arom 70%:30%	N/A	N/A	Aliph:Arom 70%:30%	N/A	Median Wax C30H62
% Carbon	81.8	N/A	83.8	81.9	N/A	N/A	81.9	N/A	78.6
% Nitrogen	0.0695	N/A	0.136	0.142	N/A	N/A	0.142	N/A	0.0769
%Hydrogen	13.5	N/A	13.9	13.3	N/A	N/A	13.3	N/A	13.5
H/C (atomic fraction)	1.98	N/A	1.99	1.95	N/A	N/A	1.95	N/A	2.07
Pentane insolubles (C5)	0.21% (C5)	0.06% (C5)	N/A (all)	0.19% (C5)	0.14%	N/A (all)	0.19% (C5)	0.07% (C5)	N/A (all)
Optical microscopy looking for micelles, emulsions, and precipitates	Clear brown Slight ppt	Clear brown	Yellow Soft Wax	Clear brown Slight ppt	Clear brown	Yellow Soft Wax	Clear brown Slight ppt	Clear brown	Yellow Soft Wax

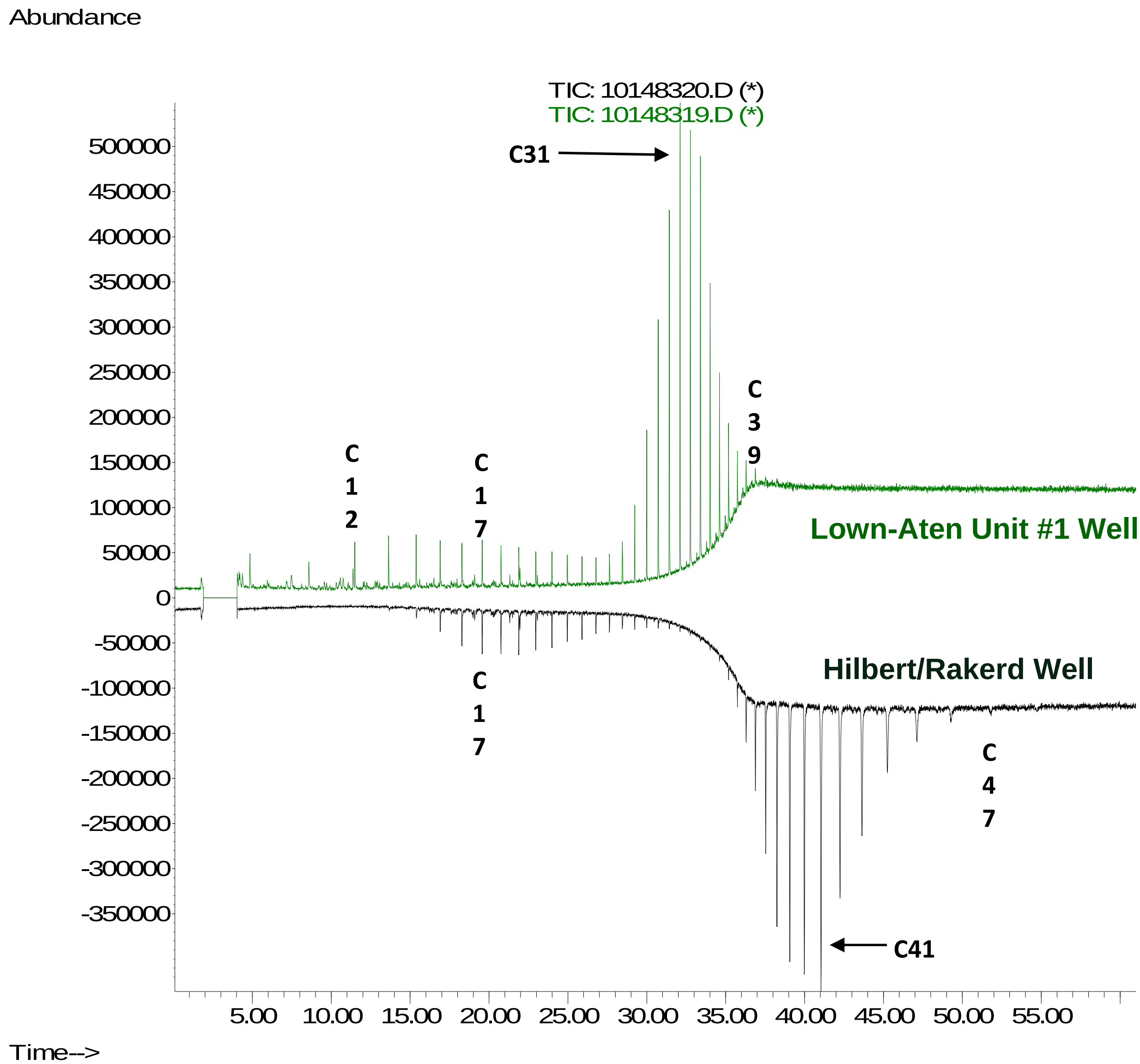

Figure 5. GC/MS Profiles of Samples 10148319 (3076550 - Lown-Aten) and 10148320 (3076554 – Hilbert/Rakerd) Paraffin Wax Deposits.

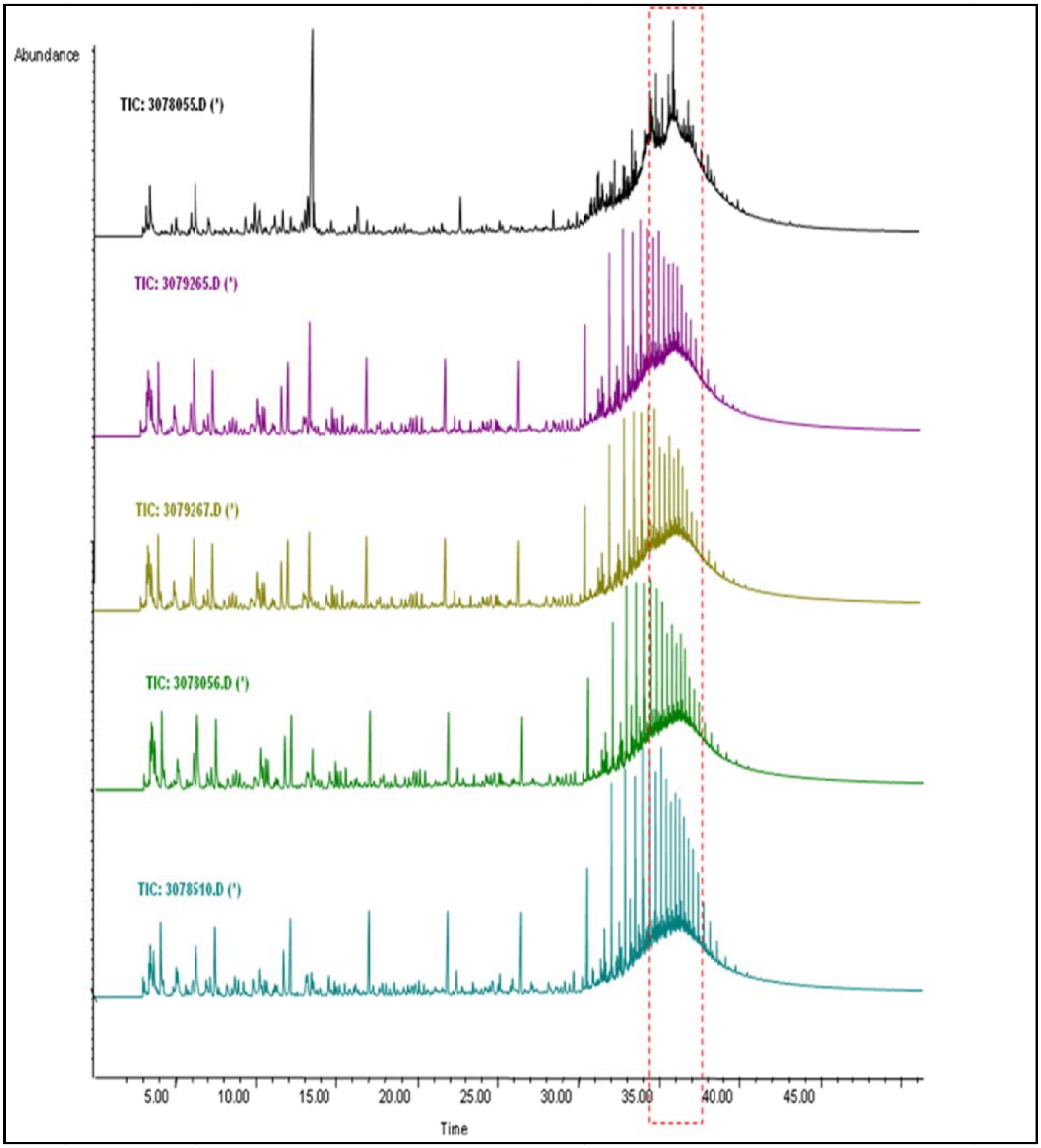

Figure 6. TIC Profile of GC/MS Analyses of Pre and Post Oil Treatment Crude oil Samples Compared to DESolv™ Treatment Oil.

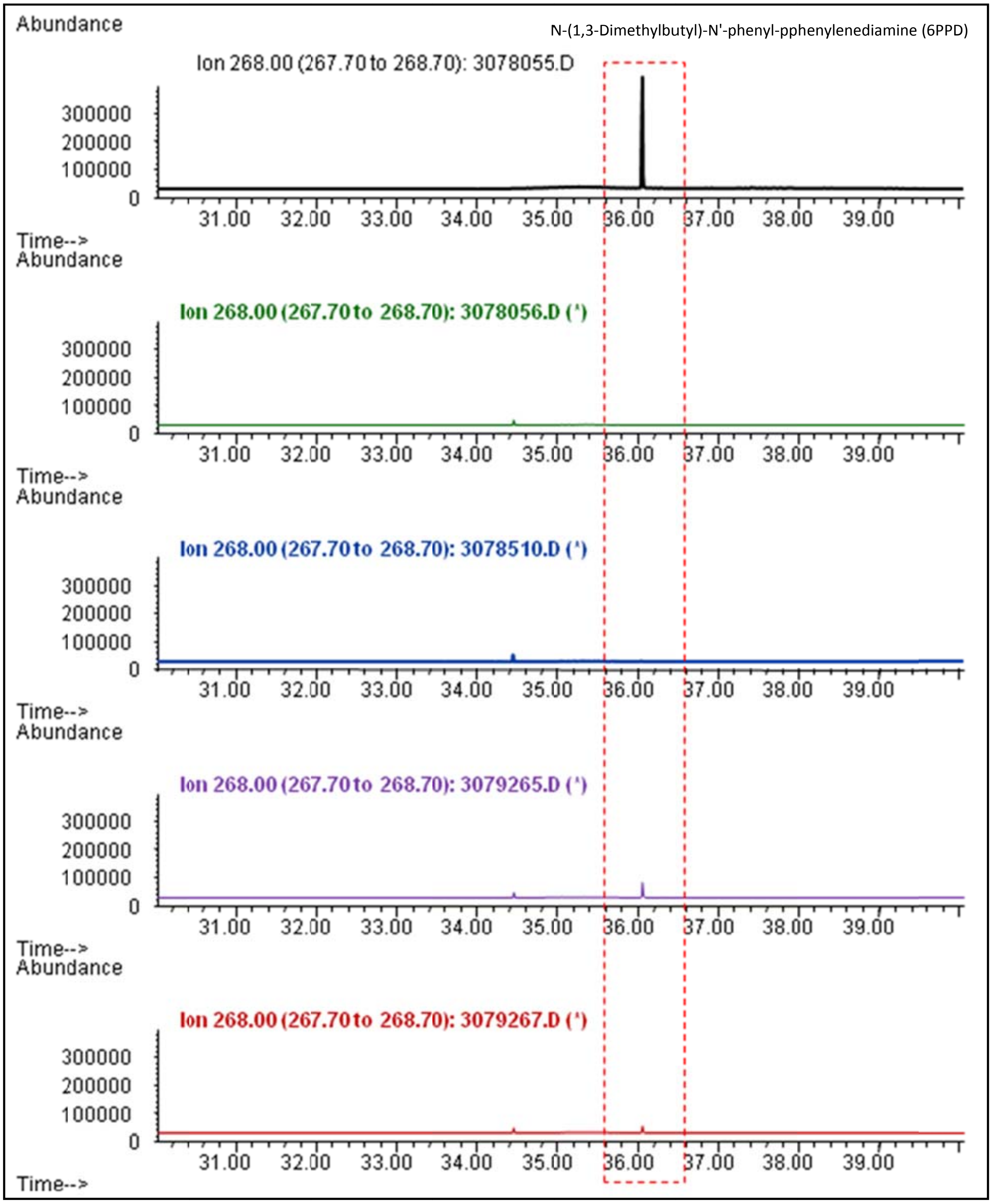

Figure 7. Selected Ion Profile of GC/MS Analyses of Pre and Post Oil Treatment Crude Oil Samples Showing 6PPD, Unique to DESolv™.

Table 3. Samples Collected (ID, Description, Location, % DESolv™)

Sample ID	Description	Location	Percent DESolv™
3078055	DESolv Pre-Treatment Sample	West Virginia	100.0%
3078056	Crude Oil Pre-Treatment Sample	West Virginia (Rakerd)	0.0%
3079265	L.Hilbert #1-a Post-Treamtment	West Virginia (Hilbert)	13.2%
3079267	T.L.Rakerd #1-a Post-Treamtment	West Virginia (Rakerd)	7.0%
3078510	Lown-Aten Unit #1 Post-Treatment	New York (Lown-Aten)	0.0%

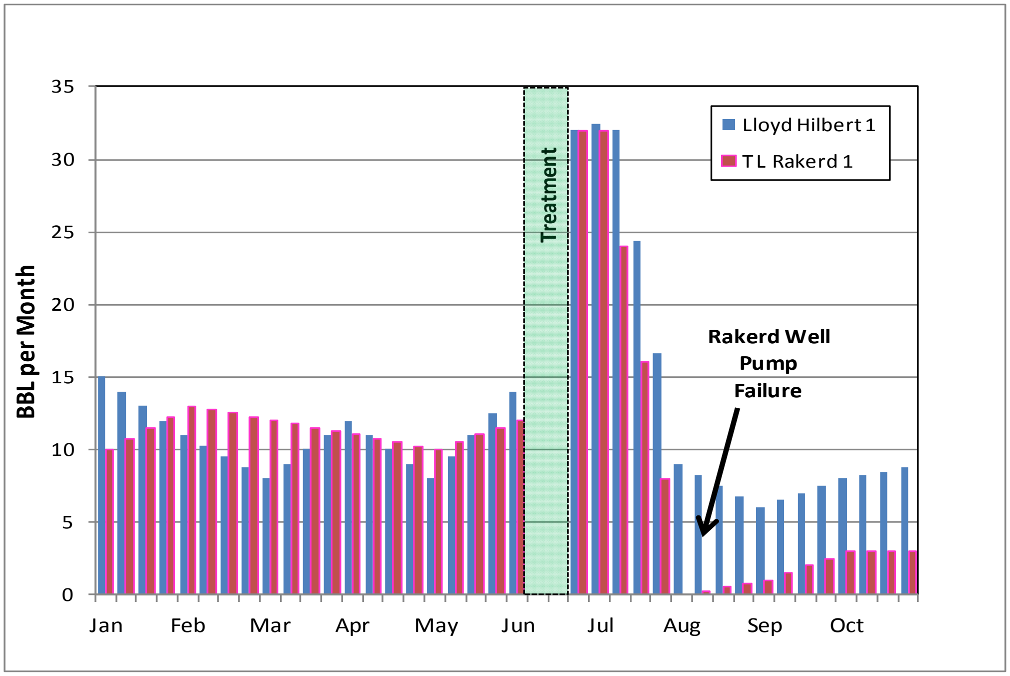

Figure 8. Oil Production Through Treatment Period in Rakerd and Hibert Wells.

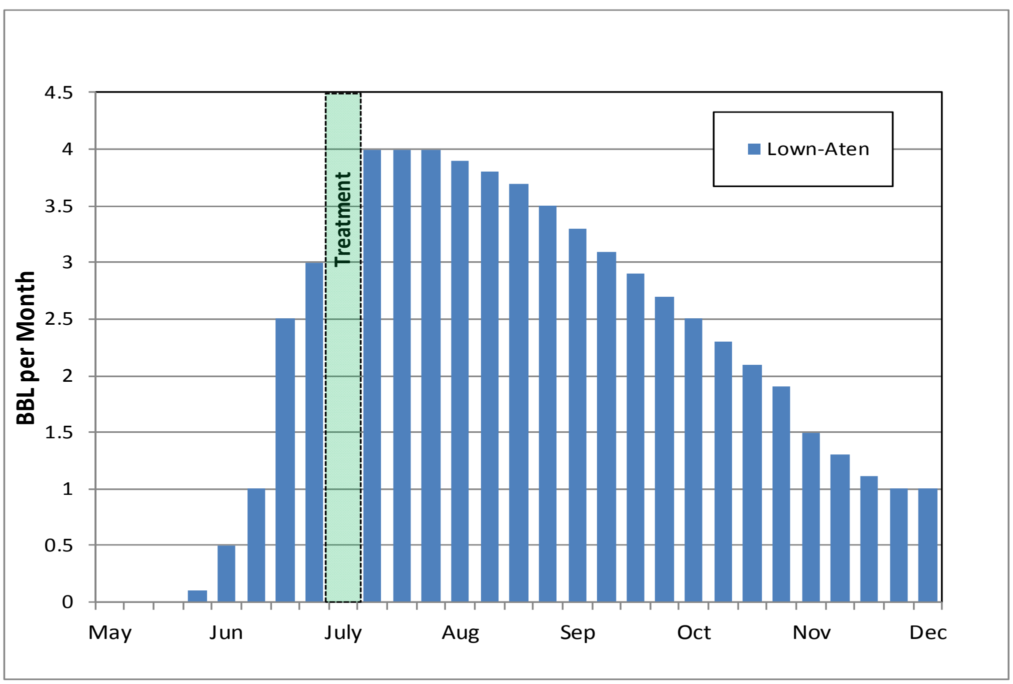

Figure 9. Oil Production Through Treatment Period in Lown-Aten Well.

4.0 Conclusion

Producing oil from stripper wells is a complicated process involving a number of different chemistries, types and properties of solidified components, formation structure, mineralogy, and porosity, flow dynamics and physical properties. The down well temperatures, pressures, and shears and their variations encountered by well fluids during flow through formations, release into reservoir spaces, movement upward, and through pumps, complicate our understanding. Well operators of stripper wells are typically not experts in chemistry or fluid dynamics but, through years of experience have developed a strong intuition for how these factors influence production from their wells.

Lown Aten LRC #317 is a well in Ellery Township Chautauqua County New York operated by Lenape Resources well in that was formed by fractured limestone reservoir that has a large pore and open structure. It produces gas, oil, and a large amount of brine. This well becomes blocked with deposits every few years, producing mostly brine at that point. When the well is shut down and then treated with a paraffin breaking solvent it starts to produce again. At the time we treated the well it had been shut down for approximately three years. Our experience with this well is that DESolv™ was pumped into the reservoir where it encountered a large portion of brine. Much of it most likely did not contact the formation and whatever did make it that far was not agitated adequately to dissolve the paraffins and penetrate the structure. It would have, then been pumped out quickly with the initiation of the production cycle. No residual DESolv™ was observed in the post-treatment crude oil sample collected several post-treatment. Although the laboratory tests showed that DESolv™ was capable of dissolving the paraffins in this well, it would not stay in the formation long enough to cause a lasting effect. The results showed an increase in production from a 3 bbl/mo rate to approximately an 80 bbl/mo rate for several months and continued to drop rapidly. Since the well was shut down for such an extended period due to extreme drop-off in production, it is difficult to determine if the treatment caused any long term improvement over the pre-shutdown condition.

T.L.Rakerd #1 and L.Hilbert #1 are oil wells in the Griffithsville Field in Lincoln Co, WV operated by East Resources Inc. Oil production in these wells has slowed over the years. Our experience with these well is that with nitrogen pressure to counter the hydrostatic pressure in the wells, all of the DESolv™ treatment penetrated into the formation in the Hilbert well and half penetrated into the formation in the Rakerd well. Oil production was observed to increase immediately after these treatments but, decreased to pre-treatment levels a few weeks later. The oil production in these wells went from approximately an 11 bbl/mo rate to approximately a 25 bbl/mo rate and lasted for under 2 months. Although subsequent treatments were not incorporated in this study, our experience is that some wells require several successive treatments to bring up levels for an extended period. An alternative approach we are testing for wells this type is to continuously pump a low level of DESolv™ down-well after the primary treatment to maintain an environment that prevents paraffins from precipitating at the formation.

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6.0 Acknowledgements

I would like to thank the following field staff for helping me understand the procedures that were followed in the field during the treatment and following. In particular discussions with John Holko were very enlightening, although treatment of his well was not effective long term; they increased our understanding of issues that have to be considered when treating wells containing large amounts of brine.

John C. Holko, President Lenape Resources, Inc
Roger Heldman, Manager East Resources
Mark Miller, field Supervisor, East Resources
Jack Crooks, field supervisor, Lenape Resourses
Duane Erickson, Director of Operations, Delta-Energy

7.0 List of Acronyms and Abbreviations

DOE	Department of Energy
RJLG	RJ Lee Group, Inc.
6PPD	N-(1,3-Dimethylbutyl)-N'-phenyl-pphenylenediamine
CHONS	Carbon, Hydrogen, Oxygen, Nitrogen, Sulfur Analyses
GC/MS	Gas Chromatography / Mass Spectometry
ICP	Inductivly Coupled Plasma Spectroscopy
DESolv™	Delta-Energy Solvent
H/C	Hydrogen/Carbon