Nd-FC POLYMERIZATION

Method Summary:
This method describes the method for the Polymerization of Butadiene using a Neodymium pre-formed catalyst (Neodymium Finished Catalyst): **COMCAT Nd-FC (0.06 mol/l)**

LEGAL DISCLAIMER :
Comar Chemicals (Pty) Ltd provides this procedure only as a guideline to ensure the most accurate use of its catalyst. Comar Chemicals (Pty) Ltd accepts no responsibility or liability for any loss or damage of whatever nature (direct, indirect, consequential or other) arising from the use or handling of its catalyst or materials and processes according to this procedure.

Apparatus:
Refer to Appendix -1.

Reagents:
Refer to Appendix-2 (Detailed)

- Hexane
- 10% Diisobutyl Aluminium Hydride (DIBAH)
- Butadiene (BD)
- Neodymium Finished Catalyst (NdFC)
- Anti-oxidant – Irganox 1520
- Bottle Nitrogen
- Molecular Sieves – Grade 3A
- Activated Alumina
- Ethanol (>95%)
- Sodium Metal
- Caustic Solution (10%)
- Exxal 13 Alcohol
- Concentrated Sulphuric acid
- Ethylene glycol/water mixture 50:50

Safety Regulations:

Protective Equipment

- Due to the pyrophoric nature of the alkyl aluminium compounds, and the flammability of the hexanes and butadiene, all handling and processing of these compounds must be done in an appropriately rated fume cupboard and enclosures, fitted with nitrogen

supply and extraction capabilities.

- PPE rated for handling alkyl-aluminium compounds must be donned.

Chemicals

- **Hexane –** Highly flammable liquid and vapour. May be fatal if swallowed and enters airways. Causes skin irritation. May cause drowsiness or dizziness. Suspected of damaging fertility. May cause damage to organs through repeated and prolonged exposure. Central Nervous system and Peripheral Nervous system. Very toxic to aquatic life.

- **10% Dibah** – Highly flammable liquid and vapour. In contact with water releases flammable gases which may ignite spontaneously. Catches fire spontaneously if exposed to air. Causes severe skin burns and eye damage. May cause drowsiness or dizziness. Suspected of damaging fertility.

- **Butadiene –** Extremely flammable liquefied gas. Highly volatile, when released it will disperse as a highly flammable vapour cloud. Contact with liquefied gas may cause frostbite. May form explosive peroxides on exposure to air. Excessive inhalation of this material causes headaches, dizziness, nausea and loss of coordination. Contains a component that may cause cancer.

- **Comcat NdFC** – Highly flammable liquid and vapour. In contact with water releases flammable gases which may ignite spontaneously. Causes severe skin burns and eye damage. May cause drowsiness or dizziness. Suspected of damaging fertility or the unborn child. Toxic to aquatic life.

- **Irganox 1520 –** Not classified as hazardous.

- **Bottle Nitrogen Gas -** Contains gas under pressure. In high concentrations may cause asphyxiation (example in a confined spaces). Symptoms may include loss of mobility or consciousness. Victim may not be aware of asphyxiation.

- **Molecular Sieves (Grade 3A) –** May cause irritation to skin, eyes and respiratory tract.

- **Activated Alumina -** May cause irritation to skin, eyes and respiratory tract.
- **Ethanol –** Causes serious eye irritation. Avoid inhalation of vapour/mist.
- **Sodium Metal –** Highly flammable and corrosive. In contact with water releases flammable gasses which may ignite spontaneously. Causes severe skin burns and eye damage.
- **Caustic Solution (10%) –** Causes severe skin burns and eye damage. Do not breathe mist, spray or vapours.
- **Exxal 13 Alcohol –** Not classified as hazardous.
- **Concentrated Sulphuric Acid –** May be corrosive to metals. Causes severe skin burns and eye damage.
- **Ethylene glycol/water mixture 50:50 –** Harmful if swallowed. Causes skin and eye irritation.

Preparation: (Note – Use ONLY Nitrogen purity > 99.999%)

1. Clean Reactor Vessel as described in Appendix-3(A)
2. Clean Syringes as described in Appendix-3 (B)
3. Fill polymer sample bottles with approximately 50 ml of a 1% mixture of anti-oxidant (Irganox-1520) in Ethanol and weigh and record the total mass. Prepare a Batch Sheet and enter data as described in Batch Sheets in Appendix-5.
4. Draw 10% Dibah and NdFC catalyst from canisters according to method CC065C

Procedure:

A: HEXANE DEHYDRATION / DISTILLATION

Refer to Appendix-4 (B)

1. Purge entire hexane distillation system and hexane storage bottle for 30 minutes by opening nitrogen (set at 50kPa) to the flask and venting through the condenser outlet.
2. In a 5-litre glass bottle, add 100ml concentrated Sulphuric acid in 5000 ml plant hexane and agitate well for 30 minutes. Allow this to settle overnight, and decant the hexane supernatant into another dry 5 litre glass bottle. Discard the waste sulphuric acid. Charge the distillation flask to a level of approximately 4,5 litres of this hexane under N2 blanket, then add 50 ml of 10% Dibah to the distillation flask. Stopper the flask.

3. Open the cooling water to the condenser.
4. Ensure that the valve to the "collection vessel" is closed.
5. Start the heating mantle to bring the hexane to gentle boiling and constant refluxing.
6. Continue refluxing for at least 2 hours, while intermittently tapping off top distillate fraction from the reflux collection reservoir (hourly).
7. Thereafter, open the valve to the collection vessel slightly to allow dry hexane to drip-feed into the collection vessel, while still refluxing simultaneously.
8. Once the Collection vessel is full, close the hexane feed and pressurise the hexane from the Collection Vessel into the 10-litre glass Storage Vessel.
9. Then re-open the valve to feed the empty Collection Vessel.
10. Continue the dehydration process until approximately 4 litres of hexane has been transferred to the Storage vessel.
11. Switch off the heating mantle and allow the flask contents to cool under nitrogen.
12. Switch off the Cooling water and nitrogen supply once the contents of the flask are below 30 deg.C.
13. The remaining Dibah/hexane solution in the boiling flask can be removed and discarded appropriately.
14. Once the 10L glass storage vessel is full, add 5 cubes of the Sodium metal, this must be thoroughly cleaned in hexane prior to adding to the dry hexane.
15. Purge with nitrogen (typically 2L hexane loss per 10L hexane) until deoxygenated. Leave overnight to stand prior to polymerisation. This can be made in advance and stored under Nitrogen.
16. Transfer the dry hexane from the 10L Glass storage bottle into the 2L hexane-charging canister.
17. H2O< 5ppm ("no-titration") indicated by Karl-Fischer volumetric titration (typically <5 ppm by Coulometric K-F).
18. Alternatively, bulk hexane distillation can be carried out in the plant – Refer SOP-QEH186. The distilled hexane is then decanted in Nitrogen purged drums/kegs. The hexane is then transferred to a 10L Glass Media Bottle and steps 15-18 is implemented thereafter.

B: BUTADIENE (BD) PURIFICATION – CCAG (Refer to CC091 for COMAR):

Refer to Appendix-4 (C)

B-1: Preparation

1. Fill TK-001 and the Heater bath with potable water.
2. Fill TK-002 and the Chiller bath with glycol/water mixture.
3. Fill TK-004 with <u>one litre</u> of 10% NaOH solution (can be done by drawing solution from a beaker by vacuum when piping is disconnected)

4. Fill TK-005 with <u>one litre</u> of deionised water (can be done with drawing by vacuum when piping is disconnected similar manner as with NaOH)
5. Fill Molecular sieve in cylinder before the flow-meter (flow meter pre-drier), and in column COL-001
6. Fill Activated alumina in column COL-002
7. Close all fittings and vessels and pressure-test the system with nitrogen at 4 bar.g pressure.

B-2: Inertization

1. For every time that the unit has been opened to replenish the preparation items described in Section-B-1, the unit has to be properly de-oxygenated with inert gas (nitrogen) purging.
2. The inertization process is preferably be done with the Purified BD cylinder (TK-006) empty, but this can be by-passed if TK-006 still has usable purified BD in it. TK-007 can be disconnected and independently purged.
3. Open V-001 and set the N2 regulator (PCV-001) to 4 bar.g pressure.
4. V-007& V-008 should be closed and only used when distilling. Close V-006, V-015, V-021.
5. Open V-002, V-003, V-014, V-016, V-017, V-020, V-019, V-024
   This allows the N2 to purge the columns and the collection vessel TK-006 and vent to atmosphere.
   Allow this purging to proceed for 3 hours minimum.
6. Thereafter, close V-014, V-016, V-017, V-019 and V-003
7. Open V-006, V-009 (normally always open), V-010 and regulate flow at 50% of flow-meter scale by opening V-012.
   This allows N2 to de-oxygenate the NaOH solution and wash-water and vent to atmosphere.
   Allow this purging to proceed for 3 hours minimum.
8. <u>Close all valves</u> except V-009.

B-3: Start-up and purification

1. With TK-003 (Inhibited BD Cylinder) installed, open V-008, V-010, V-012 (fully open), V-014, V-016, V-017, V-020, V-019, V-024.
2. Start the circulation through the water heater set at 35 deg.C until steady levels in the water bath TK-001 and the water heater tanks are achieved.
3. Start the circulation through the chiller (at the same time as starting the heater circulation), set at minus 20 deg.C until steady levels in the bath TK-002 and the chiller tanks are achieved.
4. Once the bath temperatures have reached set points, slowly open V-007 partially to regulate a flow of approximately 20% of the full scale of the flow meter, while venting the residual nitrogen from the system through the VOC vent. Allow the BD to flow to vent for approximately 2-5 minutes, then close V024 and V-019.
5. BD will then condense into TK-006.
6. Once TK-006 is full, the flow meter will indicate a reduced flow and eventually a zero flow.

7. Purified BD can be drawn from TK-006 by opening V-021, quick-coupling TK-007, and slightly vent TK-007 to allow the filling. Once desired mass is obtained in TK-007, close V-021 and un-couple TK-007.

B-4: System shut-down:

1. If the system is not planned to be used for over a week, then the system needs to be purged of BD to avoid any polymer formation in the pipelines and columns.
   Any purified BD in TK-006 can be stored at approximately 5 deg.C or lower for 2 weeks maximum. Thereafter this must be discarded as it may contain high VCH content and may possibly start forming “pop-corn” polymer as well as undesired peroxide formations which can lead to an explosion.
2. Close valves V-007, V-008, Close V-017 if TK-006 purified BD needs to be stored.
3. Shut down the Heater and the Chiller units.
4. Open V-024, V-001, V-006, V-010 and regulate the N2 flow at 50% scale of the rotameter, to flow through the Mol-sieve column and the Activated alumina column to vent to atmosphere. Purge for 6 hours, then close all valves.

C-1: CHARGING HEXANE TO REACTOR

1. Transfer dry hexane from the 10L Hexane storage bottle into the 2 litre Hexane Charge canister using nitrogen at approx. 50kPa.
2. Nitrogen Purge the Catalyst and Dibah bombs for 10 minutes prior to use. Always keep under Nitrogen pressure, min. **2 bar.g**.
3. Transfer exactly 15g dry hexane from the 2L hexane charge canister into 2x 75ml charging cylinder (for the scavenging DIBAH and catalyst diluent). Place Dibah and catalyst bomb in glovebox.
4. Place hexane charge canister on a 4000g balance, and tare the balance.
5. Refer to the hexane charge quantity required in the batch sheet in Appendix-5.
6. Connect the quick-coupler from the Reactor inlet **Port-A** to the Hexane charge canister outlet. Connect the nitrogen supply (approx.50 kPa) to the Hexane charge canister inlet.
7. Very slowly open the N2 supply valve and the Reactor inlet valve at port-A, then open the Reactor vent valve into the oil bubbler, while hexane runs into the Reactor. Once all the hexane volume has been added, close the vent valve first, then the N2 supply, then disconnect the Hexane charge canister and weigh. If too much of hexane has been added, then convert the mass of hexane to volume (V=m/0.67). Then pressurise

the reactor to approx. 50 kPa, and remove the excess hexane volume through the sample needle point. Depressurise the reactor through the vent valve, then close the vent valve when the reactor is approx. 20 kPa.

C -2: CHARGING SCAVENGING DIBAH/HEXANE MIXTURE TO REACTOR

1. Insert one of the Charge cylinders containing 15g Hexane in the glove-box.
2. Using a Gas-tight syringe and needle, draw the required volume of 10% DIBAH (as prescribed in Section-F for the scavenging DIBAH dosage)
3. Inject the DIBAH solution into the Charge cylinder and firmly close the cylinder.
4. Shake the cylinder briefly to homogenise with the 15g hexane.
5. Remove from the glovebox and keep under nitrogen pressure prior to charging into the reactor.
6. Attach the Charge Cylinder to the Reactor Inlet quick-coupler hose. Attach the N2 feed to the Charge Cylinder with N2 supply pressure set at **2 bar.g**.
7. Open the valves to feed the DIBAH/Hexane mixture into the reactor through **Port-A**
8. When a sharp increase in reactor pressure is detected (i.e., all cylinder contents have been charged), close the Reactor inlet valve and un-couple the Charge cylinder from the reactor and from the N2 supply. Keep the empty Dibah bomb charge cylinder under Nitrogen pressure when not in use.
9. Start the agitator at speed 50% of full setting. When ready to charge BD, stop the stirrer.
10. Depressurise the reactor through the vent valve through an oil-bubbler, then close the vent valve when the reactor is approx. 20 kPa.

D: CHARGING BUTADIENE TO REACTOR

1. Tare the BD Charge cylinder on the 4000g balance.
2. Transfer BD from the Purified BD storage Cylinder which is stored in the freezer to the Charge BD Cylinder by connecting the two cylinders with quick-coupler flexible hoses. Transfer is done by pressure differential between the two cylinders until the BD Charge cylinder mass is achieved as required by the batch sheet.
3. Un-couple the Distilled BD Cylinder and attach the Charge BD Cylinder to the Reactor Inlet quick-coupler hose at **Port-B**. Attach the N2 feed to the BD Charge Cylinder and set the N2 supply pressure to **4 bar.g**.
4. Open the valves to feed the BD into the reactor.
5. When a sharp increase in reactor pressure is detected (i.e., all BD has been charged), close the Reactor inlet valve and un-couple the BD Charge cylinder from the reactor

and from the N2 supply.

6. The final reactor concentration of BD in hexane is 20% m/m BD after catalyst addition.

E: REACTOR PRE-HEATING

1. Open the Cooling water supply and return to the Reactor system.
2. Start the agitator at speed 50% of full setting.
3. Input the Set-point temperature of 65 deg.C and start to heat the contents of the reactor.
4. Monitor and record the current (amps) at 65 deg.C on the batch sheet in Appendix-5.

F: FINISHED CATALYST CHARGING:

TARGET POLYMER IS MOONEY (ML1+4) = 45 (FOR >95% MONOMER CONVERSION)

COMCAT NdFC (0,06 mol/l Nd) catalyst:

For Mooney - 45 polymer, typical recommended charge per 225g monomer batch based on Comar PARR Reactor set-up:

	mmol Nd/kg BD	Catalyst Charge Volume (ml)	mmol Scavenging Dibah/kg BD	10% Scavenging Dibah Volume (ml)	Reaction Time (min.)
NdFC/G2 (0.06 mol/l Nd)	0.659	2.47	6.87	3.28	90
NdFC/G6 (0.06 mol/l Nd)	0.659	2.47	6.87	3.28	90
NdFC/G7 (0.06 mol/l Nd)	0.659	2.47	5.97	2.85	90

- BD concentration = 20% m/m
- Reaction START temperature = 65 deg.C
- Stopper (Exxal-13) = 4,5g
- Anti-oxidant = 3,375g (10% Irganox-1520 in Hexane)

NOTE: Should REACTOR configuration vary from COMAR set-up, then a typical indicative

Mooney vs Dibah guideline could be used.

1. Transfer exactly 15g dry hexane into a 75ml charging cylinder (for the catalyst charging diluent)
   Insert the Catalyst Charge cylinder containing 15g hexane in the glove-box. Through the quick-coupler, inertise with a low flow of nitrogen, then open the cylinder cap.
2. Using a Gas-tight syringe and needle, draw (as per procedure CC065C) the required amount of catalyst.
3. Inject the catalyst into the Catalyst cylinder and firmly close the Catalyst cylinder.
4. Shake the Catalyst cylinder briefly to homogenise the catalyst with the hexane.
5. Attach the Catalyst cylinder outlet to the Reactor Inlet quick-coupler at **Port-A**.
6. Attach the N2 supply to Catalyst cylinder inlet quick-coupler.
7. Once the reactor temperature is steady at approx. **65 deg.C** (reactor pressure is typically 5 bar.g), increase the N2 supply to 9 bar.g. to the catalyst charge cylinder.
8. Switch off the heating mantle, and importantly, increase the Set Point Temperature to 120 deg.C, so that the reactor does not heat nor cool. This would enable the recording of reaction exotherms without external energy inputs or heat removals.
11. Open the N2 supply to the catalyst cylinder, then open Reactor inlet valves and allow the catalyst to run into the reactor. When a sharp increase in reactor pressure is detected (i.e., all Catalyst has been charged), close the Reactor inlet valve and de-couple the Catalyst Charge cylinder from the reactor and from the N2 supply.
12. Immediately start the timer/ stop-watch and record initial readings of time, temperature and agitator amps. Insert data in typical batch sheet in Appendix-5.

G: POLYMER SAMPLES AND DATA RECORDING

1. Increase the Nitrogen regulator pressure to 9.5 bar.g
2. Record the time on the batch sheet when the temperature begins to increase *(Reaction start time)*.
3. Draw polymer samples from the Reactor at intervals indicated on the batch sheet.
4. Sample are taken in the Ethanol/Irganox filled glass bottles, by inserting the needle at the reactor sample point at **Port-C** into the bottle septum, then opening the valve to allow the polymer/hexane mix to transfer into the glass bottle.
5. At every sample drawn, record the temperature and amps. Avoid any leakages from the bottles.
6. Shake the sample well to coagulate the polymer, then weigh the bottle with its contents. Record this total weight (bottle+Ethanol/Irganox+Hexane+BD+Polymer) in the batch sheet in Appendix-5.
7. Record the peak temperature exotherm and time of occurrence.

8. After each sample drawn, empty the needle sample point, as well as the sample dip-tube inside the reactor, by blowing nitrogen briefly in surges at 10 bar pressure.

H: BULK POLYMERISATION TERMINATION:

1. Add ~500ml Demin water to 2L of Hexane. Mix adequately for 1 hour.
2. Add 60ml of wet hexane to bomb. Add required amount of Exxal 13 to wet hexane.
3. Deoxygenate bomb for 30 minutes.
4. At the end of the reaction, charge deoxygenated Exxal13/Wet Hexane mix into reactor through the separate Exxal 13/Irganox port. Mix for 10 mins.
5. Add 60ml of wet hexane to bomb. Add required amount of Irganox to wet hexane.
6. Deoxygenate bomb for 5 minutes.
7. After 10 mins, charge deoxygenated Irganox/Wet Hexane mix into reactor through the Exxal 13/Irganox port. Mix for 5 minutes.
8. Fill another 5-litre receptacle with 1 litre of Ethanol. Run polymer straight out into 1L Ethanol and coagulate the polymer to terminate the reactions completely by "massaging" the polymer into the Ethanol for approximately 2 mins. Dry on the hot-mill as per method CC-088 for full polymer analytics.
9. In the absence of a hot-mill, dry bulk polymer in a vacuum oven set at 40 deg.C as follows. After coagulation of the bulk rubber, as much of the excess ethanol must be removed by squeezing the rubber. Weigh out ~203 grams of the rubber. **Ensure that the polymer is dried in a receptacle with a large surface area. The polymer should be weighed in a ball and then flattened out into the receptacle. This will ensure that any trapped solvent in the polymer is removed much more easily during drying.** The front glass of the vacuum oven must be covered in foil to prevent UV effects from light. The initial mass of polymer must be dried in a 40 deg.C oven under full vacuum for a period of 3hrs and at 15 min intervals thereafter until constant mass is obtained. Once the polymer is dried to a constant mass, it must be immediately packaged to avoid exposure to air and light.
10. Depressurise the reactor when empty, thereafter add approximately 800ml dry hexane into the reactor through Port A to wash reactor as described in Reactor Cleaning Appendix 3A.
11. Charge 50ml (10% Dibah) to the reactor through the Exxal 13/Irganox Port. Add the remaining 800ml Hexane through this Port.
12. Pressurise the reactor to 50 kPa with N2, then heat the hexane/Dibah to 85 deg.C.

13. Flush out the hot hexane through the sample needle until clear (hexane will be boiling as it leaves reactor). Then blow N2 through the needle discharge.
14. Cool the reactor < 30 deg.C and empty out the hexane under reactor N2 and discard the flush hexane. Repeat steps 10 to 14.
15. Add approximately 1,6 litre dry hexane into the reactor. Heat to 75 deg.C Mix and empty out the hexane under reactor N2. Repeat this washing.
16. Keep the reactor under nitrogen, in ready-state for the next polymerisation run. Prior to each poly run, pressurise the reactor to 1000kPa, then apply vacuum to -95kPa or less. Repeat this step 5X to ensure that the reactor is free of oxygen.

I: POLYMER DRYING FOR CONVERSION PLOT:

1. Pre-weigh drying dishes and number them according to the polymer samples drawn.
2. Remove the coagulated polymer samples from the glass bottles, separated from the ethanol/Irganox solution.
3. Place each polymer sample in its allocated drying dish and insert in a vacuum oven set at 100 deg.C, full vacuum.
4. Dry for approximately 1 hour to a constant weight for each sample (until all the Ethanol/Irganox, hexane and unreacted BD has been removed from the polymer).
5. Cool the samples in a desiccator, then weigh each polymer with the drying dish.
6. Deduct the weight of the drying dish and record the weights of the dry polymer.
7. Generate the conversion plot.

APPENDIX-1

APPARATUS

A. REACTOR SYSTEM:

PARR Reactor Model 4534

- 2 litre Floor Standing Reactor (Fixed Head with magnetic seal)
- With Ammeter and Control Box (speed & temp. control)
- With Heating and Cooling function and temp. sensor
- 0 – 1700 rpm pulley & 0.36 kW motor
- 6-bladed turbine impellers (2 sets)
- Nitrogen Inlet
- Pressure indicator with Pressure Safety Valve
- With dip-tube and sample extraction system.

B. SWAGELOCK CYLINDERS WITH QUICK-COUPLERS, VALVES & HOSES

- Raw Butadiene Cylinder (1 gallon / 3785 ml)
- Distilled BD cylinder (500ml)
- BD Charging cylinder (500ml)
- Catalyst Charging cylinder (1x75ml)
- Hexane Charging Bottle (2 litre Metal Canister)
- Male & Female quick-couplers
- Braided PTFE ¼" hoses
- 306SS Ball & Needle valves
- Pressure gauges
- Nitrogen pressure regulators

C. BUTADIENE PURIFICATION SYSTEM:

- 2 x Flanged column 316SS (25mm NB, 1300mm long) with ¼" inlet & outlet
- 3A Molecular Sieves
- Activated Alumina
- Oxygen Trap
- Pressure gauge
- Valves
- 316SS ¼" tubing
- Water/ glycol baths with heater and chilling systems to accommodate Raw BD and Distilled BD cylinders
- Swagelok cylinders for raw BD, NaOH solution, De-ionised water, Purified BD

D. HEXANE DISTILLATION SYSTEM:

- Heating Mantle
- 5 litre boiling flask
- 2x packed columns
- 2 litre dry hexane collection vessel
- 10 litre Dry Hexane Storage bottle
- 30 litre stainless steel storage container
- Overhead condenser and stop-cocks
- Nitrogen regulator
- Thermometer
- Tubing for N2
- 316SS ¼" tubing
- ¼" PTFE braided flexible tubing
- Quick-coupler
- Canister packed with 4A molecular sieves (1/4" inlet and outlet)
- Volumetric Karl Fischer water measurement Titrator with
  : Hydranal Composite 5 Titrant
  : Anhydrous methanol solvent

E. BALANCE:

- 4 decimal 200 g balance
- 2 decimal 4000 g balance

F. SYRINGES & NEEDLES:

- Hamilton Gas-tight syringes- graduated (20 ml, 5 ml, 1.0 ml) with PTFE plunger
- Removable threaded needles

G. GLASS BOTTLES, CAPS & SEPTA:

- 250 ml threaded glass bottles capable of 10-12 bar pressure tolerance
- Caps drilled with 3mm centre holes to fit glass bottle
- Nitrile rubber septum to fit into cap

H. GLOVE BOX:

- Perspex / glass glove box, with Nitrogen supply for inertising.

I. VACUUM OVEN

J. STOPWATCH

K. OVER-HEAD STIRRER

L. DESICCATOR

APPENDIX-2

RAW MATERIALS

A. Hexane
- Polymerization Grade or equivalent

B. 10% Dibutyl Aluminium Hydride (DIBAH) (approximate SG =0.678)
- Sourced from Albemarle, Akzo Nobel, Chemtura or equivalent as concentrated or diluted

C. Butadiene (BD)
- Industrial grade 1,3-butadiene

D. Neodymium Finished Catalyst (NdFC)
- COMCAT NdFC /0,06 mol/l Nd (sourced from Comar Chemicals)
- NdFC is either available in dilute or concentrated forms

E. Anti-oxidant
- Irganox 1520 sourced from BASF

F. Nitrogen
- Medical grade > 99.999 % purity

G. Molecular Sieves
- Grade 3A sourced from Sigma Aldrich/Zantech

H. Activated Alumina
- Sourced from Zantech

I. Ethanol
- > 95% purity industrial grade

K. Sodium Metal
- 99.9% trace metal basis sourced from Sigma Aldrich

L. Caustic Solution (10%)

M. Exxal 13
- ExxonMobil

N. Concentrated Sulphuric acid

O. Ethylene glycol/water mixture 50:50 (for the Heating and Chilling systems)

APPENDIX-3

EQUIPMENT CLEANING & PREPARATION

A. REACTOR:

1. Pressurise the reactor to 1000kPa, then apply vacuum to -95kPa or less.
2. Repeat step 1 thirty times to ensure that the reactor is free of oxygen.
3. Fill reactor with 1,6 litres of dry hexane dosed with 30 ml of NdFC/0.06mol/L. Agitate while heating the contents to 85 deg.C.
4. Cool reactor to < 30 deg.C, drain out hexane/catalyst mixture and discard appropriately.
5. Fill reactor with 1,6 litres of dry hexane dosed with 50 ml of 10% Dibah using the hexane charge canister and Dibah bomb. Agitate while heating the contents to 85 deg.C.
6. Cool reactor to < 30 deg.C, drain out hexane/Dibah mixture and discard appropriately. Repeat steps 5-6.
7. Fill reactor with 1,6 litre of dry de-gassed hexane using the hexane charge canister, then heat contents to 75 deg.C while agitating.
8. Cool reactor to < 30 deg.C under nitrogen pressure, then drain out the hexane.
9. Purge with nitrogen for 5 minutes. Keep reactor at approximately 10 kPa minimum nitrogen pressure.
10. Steps 1 - 4 are only necessary if reactor vessel has been opened for cleaning.
11. For consecutive polymerisation runs, only steps 5 to 8 are necessary after each run.

B. SYRINGE CLEANING:

1. Rinse Syringes with 10% Sodium Hydroxide solution.
2. Wash 4x with deionised water.
3. Dry in oven at 120 deg.C for 3 hours.
4. Remove from oven with gloves, and immediately purge with N2 until cool.
5. Place in a N2 blanketed desiccator and nitrogen purge prior to use.

APPENDIX-4

PHOTOS & DRAWINGS

A. REACTOR SYSTEM:

Fig -1. 2 litre PARR reactor

Fig-2. Reactor Enclosure Fume hood

Fig-3. Hexane charging to reactor

Fig-4. Butadiene charging to reactor

Fig-5. Reactor Controller

Fig-6. Catalyst & Scavenging Dibah charging to reactor

Fig-7. Polymer drawing from reactor for Conversion plot

Fig-8. Bulk polymer discharge from reactor bottom

B. HEXANE DISTILLATION SYSTEM:

Fig-9. Hexane Distillation

Fig-10. Comar Dry Hexane Storage

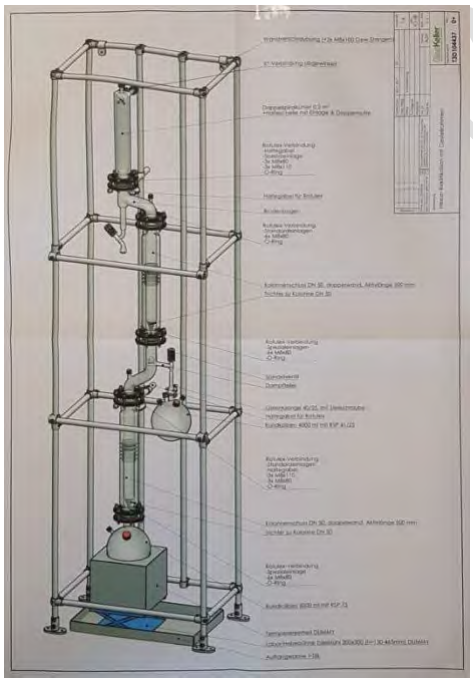


Fig-11. Hexane Distillation diagram

Fig-12. Hexane Distillation system

C. BUTADIENE PURIFICATION SYSTEM:

Fig-13. Butadiene Purification system

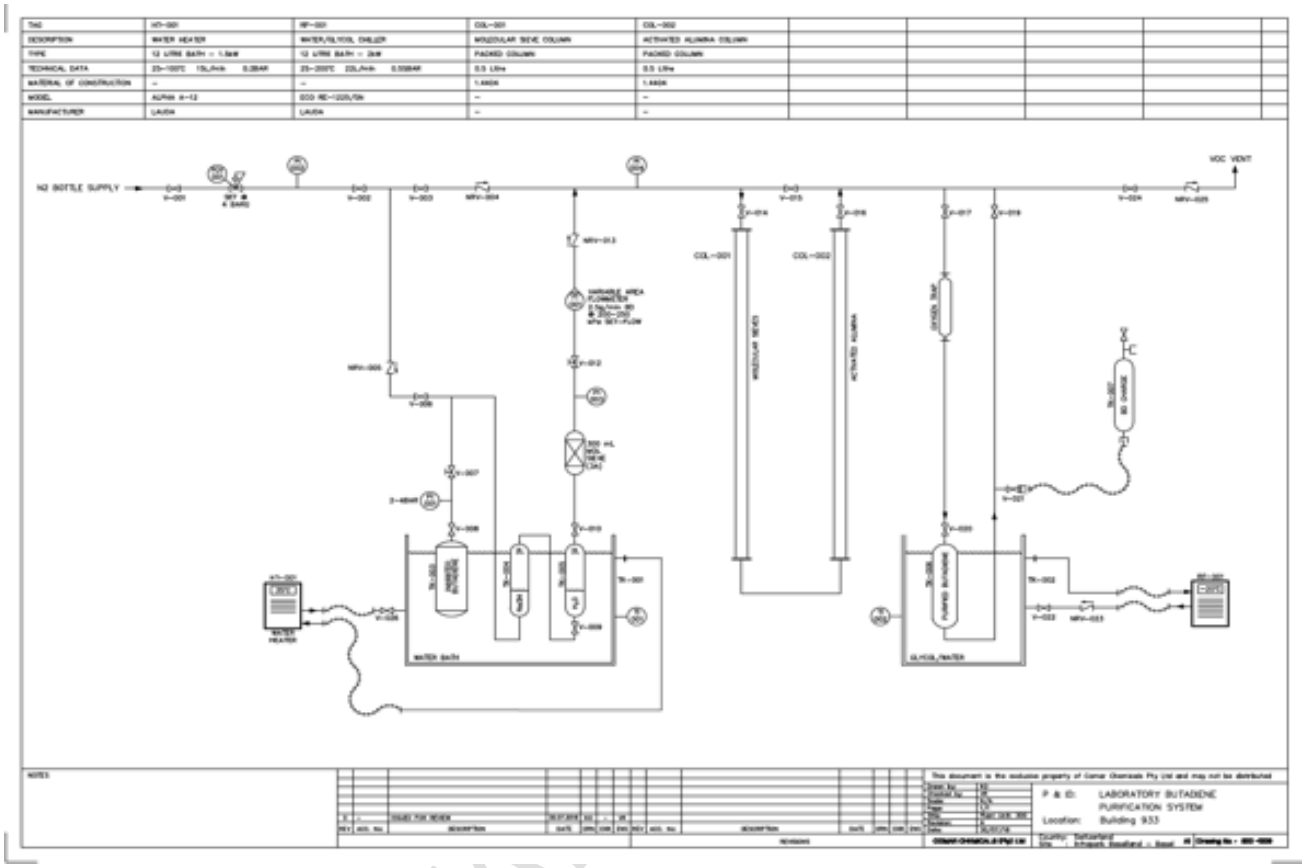


Fig-14. Butadiene Purification Diagram

D. BOTTLES, CAPS, SEPTUM, SYRINGES & NEEDLES:

Fig-15. Coagulating bottle for conversion

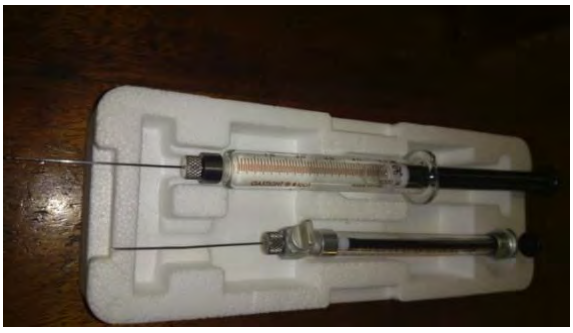


Fig-16. Gas-tight syringes

E. SWAGELOK CYLINDERS & QUICK-COUPLERS:

Fig-17. Swagelok Cylinders

Fig-18. Swagelok Quick-connects

F. GLOVE-BOX & KARL-FISCHER TITRATOR:

Fig-19. Inert Glove Box

Fig-20. Karl Fischer Titrator

G. POLYMER SAMPLES (Coagulated & dried):

Fig-21. Coagulated polymer in Ethanol

Fig-22. Dried bulk polymer

H. POLYMER ANALYTICAL INSTRUMENTATION

Fig.23. GC Chromatography

Fig.24. GPC

Fig.25. FTIR

Fig.26. Mooney Viscometer

Fig.27. Roller mill (heated)

APPENDIX-5

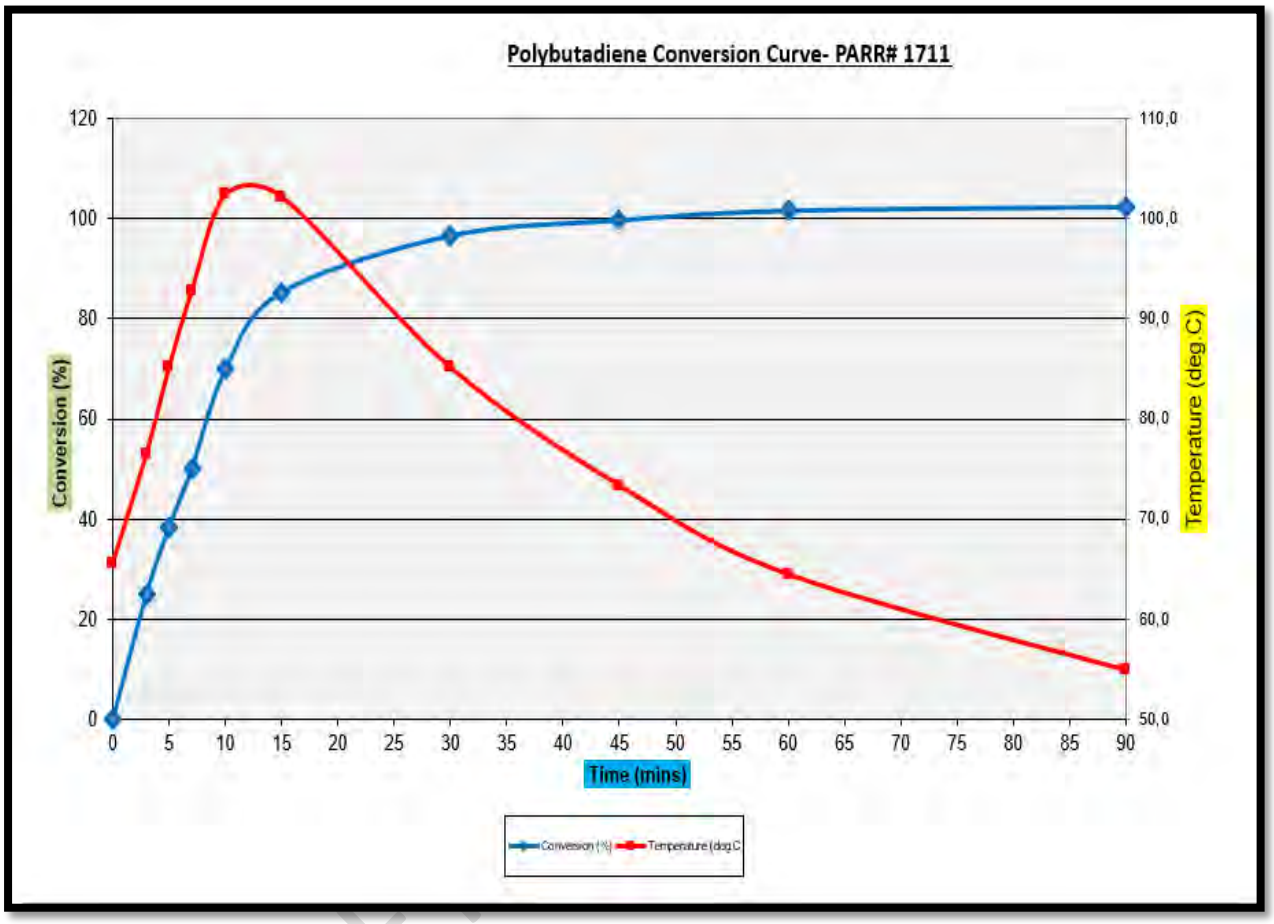
TYPICAL BATCH SHEETS

A. POLYMERISATION BATCH SHEET AND CONVERSION PLOTS (NdFC-G7 CATALYST):

PARR REACTOR POLYMERISATION

DATE :	2023/10/03			Nd-FC	0,0601	mol/L	B/No : NdFC/G7/011023		
				SG	0,731				
File		PARR 1711		CATALYST DESCRIPTION : Finished Catalyst : Pre-formed					
REACTION TIME (min) :		30							
BD LOADING (g):		225		BASIS	Nd:Cl:Al	1Nd : 2.7Cl : 13.2Al			
HEXANE LOADING (g) :		900		Charge rate equivalent kg NdV/T on PBR		0,4363			
BD CONCENTRATION (%m/m)		20,000		Charge rate equivalent	mmol Nd/kg BD	0,659	al concentration of scavenging Dibah		9,88
CATALYST CHARGE (ml):		2,47		Reaction Start Time (:			SG of 10% DIBAH		0,678
Hexane in charging bombs									
Dibah Bomb (g)	13		Hexane/010623		Vol Dibah to add (ml	2,85	mmol scav Dibah/kg BD =		5,9661
Catalyst Bomb (g)	13		BD/020923		use 2,5ml syringe & sep		mmol scav Dibah / mmol Nd =		9,0574
Balance Hexane to add to Re	674						Total mmol Dibah (cat + scav) / kg BD		14,6609
							Total mmol Dibah (cat + scav) / mmol Nd		22,2574

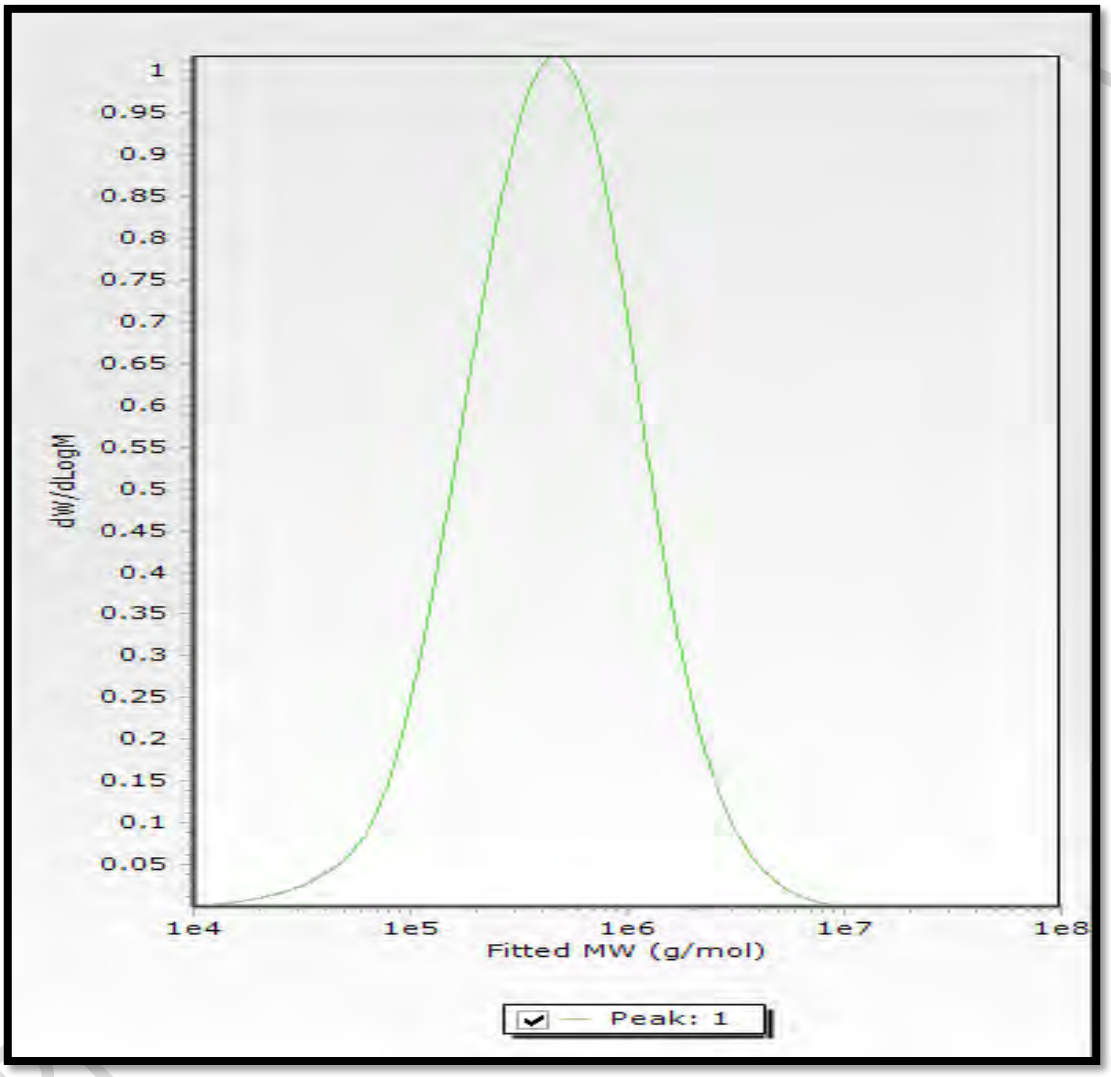
Sample #	Poly Time (min)	Peak Temp	Temp (deg.C)	Current (amps)	Bottle mass/IPA (g)	Bottle & sample (g)	Dry PBR (g)	Conversion (%)	
Start condition	0		65,5	0,63				0	STOPPER (g)
1	3		76,5	0,63					4,5
2	5		85,1	0,63	192,69	220,22	2,112	38,35	
3	7		92,7	0,63					IRGANOX 102
4	10		102,4	0,76	193,87	213,29	3,272	63,84	5,375
5	15		102,2	0,84	193,14	209,82	2,846	85,30	
6	30		85,1	0,93	191,56	196,44	0,3430	36,62	
7	45		73,3	0,34	190,81	193,36	0,6280	33,68	
8	60		64,4	1,02	193,00	197,49	0,3122	101,58	
9	90		54,8	1,05	188,3	191,89	0,7347	102,33	
								#DIV/0!	
Peak Temp	12	103,8	Delta Amps	0,36					
MOONEY	43,7								
SR	-0,6633								


Polybutadiene Conversion Curve- PARR# 1711
Conversion (%)
Temperature (deg.C)
Time (mins)
120
100
80
60
40
20
0
110,0
100,0
90,0
80,0
70,0
60,0
50,0
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90

APPENDIX-6

TYPICAL POLYMER CHARACTERISTICS

A. MOLECULAR WEIGHT DISTRIBUTION:



Sample Name	Mp	Mn	Mw	Mv	Mz	Mz+1	PD	Mooney	SR	Cis	Trans	Vinyl	PE (deg.C)	Rxn Time (min.)	mmol Nd/kg BD	mmol Scav.Dibah /kg BD
Parr#1711	465393	285411	657599	1247041	1382754	2566069	2,304	43,7	-0,6693	97,83	1,69	0,48	103,8	90	0,659	5,97

APPENDIX-7

A. TYPICAL GC ANALYSIS FOR HEXANE

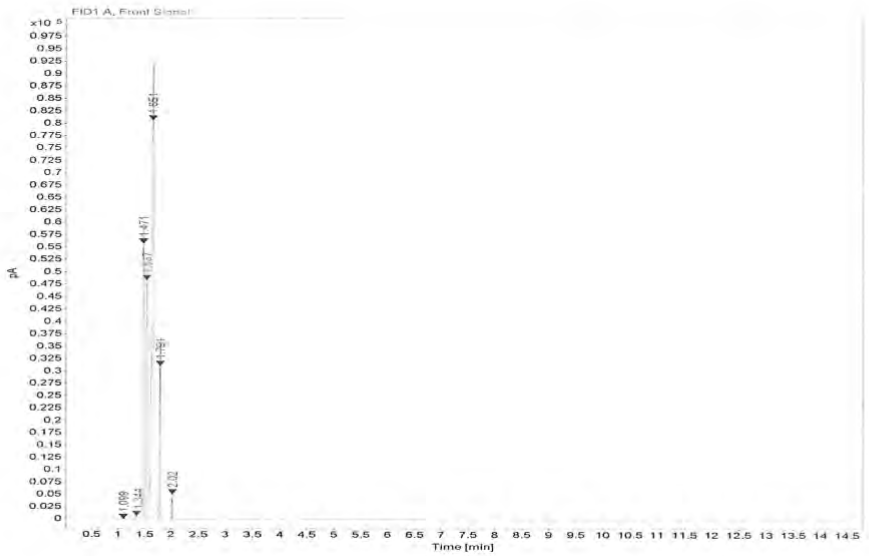
Area Percent Report

Agilent Technologies

Data file: C:\CHEM32\1\DATA\HEXANE\HEXANE DRUM 11.D
Sample name: Hexane Drum 11
Description: Hexane - Drum 11
Sample amount: 100.000
Sample type: Sample

Instrument: Agilent 7890 GC
Injection date: 3/11/2020 10:33:48 AM
Acq. method: HEXANE DB1.M
Analysis method: HEXANE DB1.M
Last changed: 2/26/2020 4:13:52 PM

Location: Vial 101
Injection: 1 of 1
Injection volume: 0.500
Acq. operator: SYSTEM



Area Percent Report

Agilent Technologies

Signal: FID1 A, Front Signal

RT [min]	Type	Width [min]	Area	Height	Area%	Name
1.099	BB	0.0121	3.1886	4.6066	0.0008	
1.344	VB	0.0152	536.5621	616.3788	0.1332	
1.471	BV S	0.0241	87165.6953	56119.9766	21.6417	
1.537	VV S	0.0232	69833.2422	50191.7891	17.3384	
1.651	VV S	0.0394	191995.6406	81156.6016	47.6691	
1.791	VV S	0.0231	48515.2227	31312.2891	12.0455	
2.020	VB S	0.0155	4717.6387	5264.7397	1.1713	
		Sum	402767.1901			

B. TYPICAL GC ANALYSIS FOR PURIFIED BUTADIENE

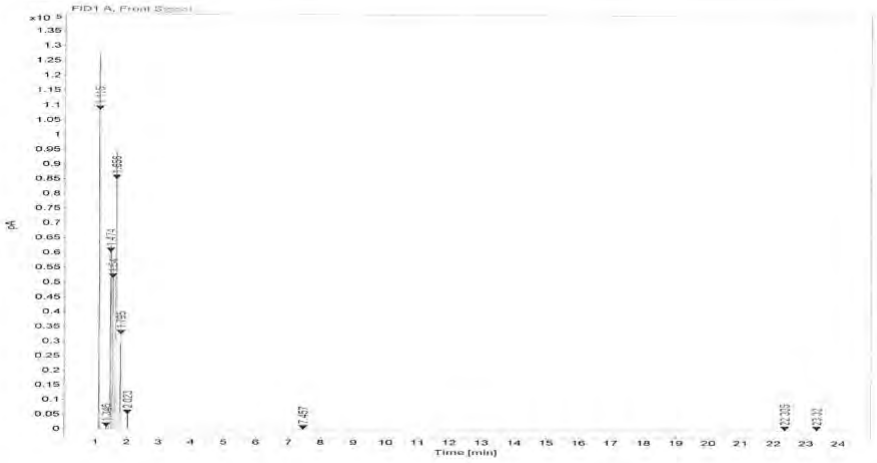
Area Percent Report

Agilent Technologies

Data file: C:\CHEM32\1\DATA\HEXANE\BD020320 IN HEX15.D
Sample name: 15% BD/020320 in hexane
Description: 15% BD/020320 in Drum hex 11
Sample amount: 100.000
Sample type: Sample

Instrument: Agilent 7890 GC
Injection date: 3/13/2020 9:27:38 AM
Acq. method: HEXANE DB1.M
Analysis method: HEXANE DB1.M
Last changed: 3/13/2020 9:25:16 AM

Location: Vial 101
Injection: 1 of 1
Injection volume: 0.500
Acq. operator: SYSTEM



Area Percent Report

Agilent Technologies

Signal: FID1 A, Front Signal

RT [min]	Type	Width [min]	Area	Height	Area%	Name
1.115	BV S	0.0135	74864.6875	103141.7734	14.2951	
1.346	VV X	0.0160	689.9565	731.5201	0.1317	
1.474	VV S	0.0262	101833.9766	62031.3242	19.4448	
1.540	VV S	0.0264	79398.5000	50095.5156	15.1608	
1.656	VV S	0.0369	209516.8750	84483.7578	40.0063	
1.795	VV S	0.0237	52439.0898	32711.7461	10.0130	
2.023	VB S	0.0166	4891.2881	4919.3125	0.9340	
7.457	BB	0.0221	3.1302	2.2639	0.0006	
22.335	VB	0.0263	4.0738	2.4637	0.0008	
23.320	BB	0.0269	67.5091	39.5159	0.0129	
		Sum	523709.0865			

NOTES :

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