Towards Sustainable Continuous Production of Azo Dyes: Possibilities and Techno-Economic Analysis

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Supporting Information

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S1. General Information

General Information

All the reagents and solvents used were commercial-grade (above 98% purity). Aniline, sodium nitrite, sodium hydroxide, hydrochloric acid (35% w/w), β-naphthol, 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one and sodium carbonate were purchased from Alfa Aesar and Merck Life Science Pvt. Ltd. Longer BQ50-1J peristaltic pumps were used for pumping aniline hydrochloride and sodium nitrite solutions. Longer BT100-2J pump was used to pump the coupler solution. A jacketed tubular reactor (Tube side: Teflon, 1/8 inch OD, 2 mm ID and 15 mL & Jacket Shell of SS316) was used for diazotization reaction with a residence time of 2 min.[1] A jacketed glass bubble column reactor (~ 53 mL active volume) with residence time ~ 2.5 min was used for the azo coupling reaction. A sintered disk was used as a sparger and two Longer BT300-2J pumps at 600 mL/min each was used for passing air into the bubble column reactor. Utility temperature was kept at 2 ^{o}C by using a thermostat (Julabo FP50) for all the experiments. Buchner funnel vacuum filtration assembly was used for separating the solid product. The product was air-dried and analyzed using NMR without any further purification. All experiments were repeated more than three times to ensure reproducibility. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-200 MHz instrument with TMS as an internal standard. Chemical shifts are given in ppm (δ), referenced to tetramethyl silane (TMS) for ^{1}H NMR and ^{13}C resonances of $CDCl_3$ (δ=77.0 ppm) for ^{13}C NMR as internal standards. Data are represented as follows: chemical shift, multiplicity (s =singlet, d = doublet, t = triplet, m = multiples, b = broad, respectively) coupling constant (Hz), and integration.

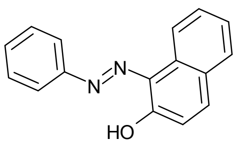
General Procedure for Feed Solution Preparation

Aniline (1.0 equiv.) is suspended in water (25.0 equiv.) and maintained below 5 ^{o}C using an ice bath. 35% Hydrochloric acid (3.0 equiv.) is added slowly under stirring conditions. After the addition is complete the solution is stirred for 5-10 min. Sodium nitrite (1.05 equiv. - 1.1 equiv.) was dissolved in water to get a 10% w/w solution. The resulting molarity of the feed solutions of aniline hydrochloride salt and sodium nitrite solutions were 1.21 M and 1.5 M respectively. For the case of Sudan-I dye, β-Naphthol and sodium hydroxide were used as coupler and base respectively. Sodium hydroxide (3.0 equiv.) was dissolved in water (157.0 equiv.) under ice-cold conditions *(Caution:*

Dissolution process is highly exothermic). β-Naphthol (1.05 equiv.) was dissolved in the above solution to give the coupler feed solution of concentration 0.35 M. For the case of Solvent Yellow 16, 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one and sodium carbonate were used as the coupler substrate and base respectively. Sodium carbonate (2.0 equiv.) was dissolved in water (168.0 equiv.) of water. 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one (1.05 equiv.) was dissolved in the above solution. The solution was sonicated to enhance the dissolution process. The feed solution concentration was 0.32 M. The feed solutions were precooled continuously during the experiment using an ice bath or a coiled heat exchanger (in the case of coupler solution).

Continuous Flow Synthesis of Azo Dyes using Bubble Column Reactor

Sudan I Dye

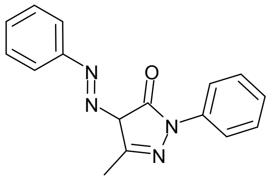


The flowrate for aniline hydrochloride, sodium nitrite, and coupler solution was 4.1 mL/min, 3.41 mL/min, and 14.92 mL/min respectively. The steady-state product was filtered for ~ 27 min and dried to yield 31.58 g (92.04 ± 3.50 %) of the Sudan I product as reddish-orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.26 (s, 1H), 8.58-8.56 (m, 1H), 7.75 (m, 1H), 7.73-7.71 (m, 2H), 7.61-7.59 (d, *J* = 7.75 Hz, 1H), 7.58-7.53 (m, 1H), 7.51-7.46 (m, 2H), 7.42-7.38 (m, 1H), 7.32-7.28 (m, 1H), 6.88-6.86 (d, *J* = 9.50 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.99, 144.77, 140.12, 133.61, 130.09, 129.61, 128.89, 128.64, 128.08, 127.44, 125.74, 124.86, 121.73, 118.59.

Solvent Yellow 16



The flowrate for aniline hydrochloride, sodium nitrite and coupler solution was 4.1 mL/min, 3.41 mL/min, and 16.46 mL/min respectively. The steady-state product was filtered for ~ 27 min and dried to yield 36.11 g (96.60 ± 2.18 %) of the Solvent Yellow 16 product as bright yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 13.58 (s, 1H), 7.97-7.94 (m, 2H), 7.45-7.39 (m, 6H), 7.23-7.18 (m, 2H), 2.37 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.81, 148.61, 141.16, 138.06, 129.69, 128.94, 128.53, 125.83, 118.60, 115.84, 11.81.

S2. Continuous Flow Setup & Process Flow Diagram for Azo Synthesis

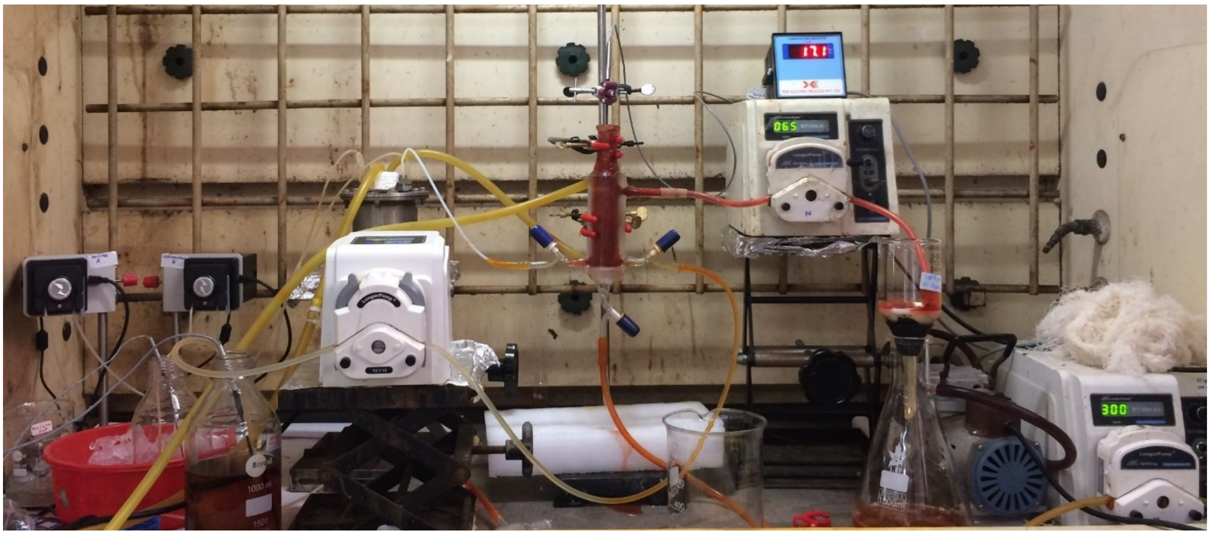
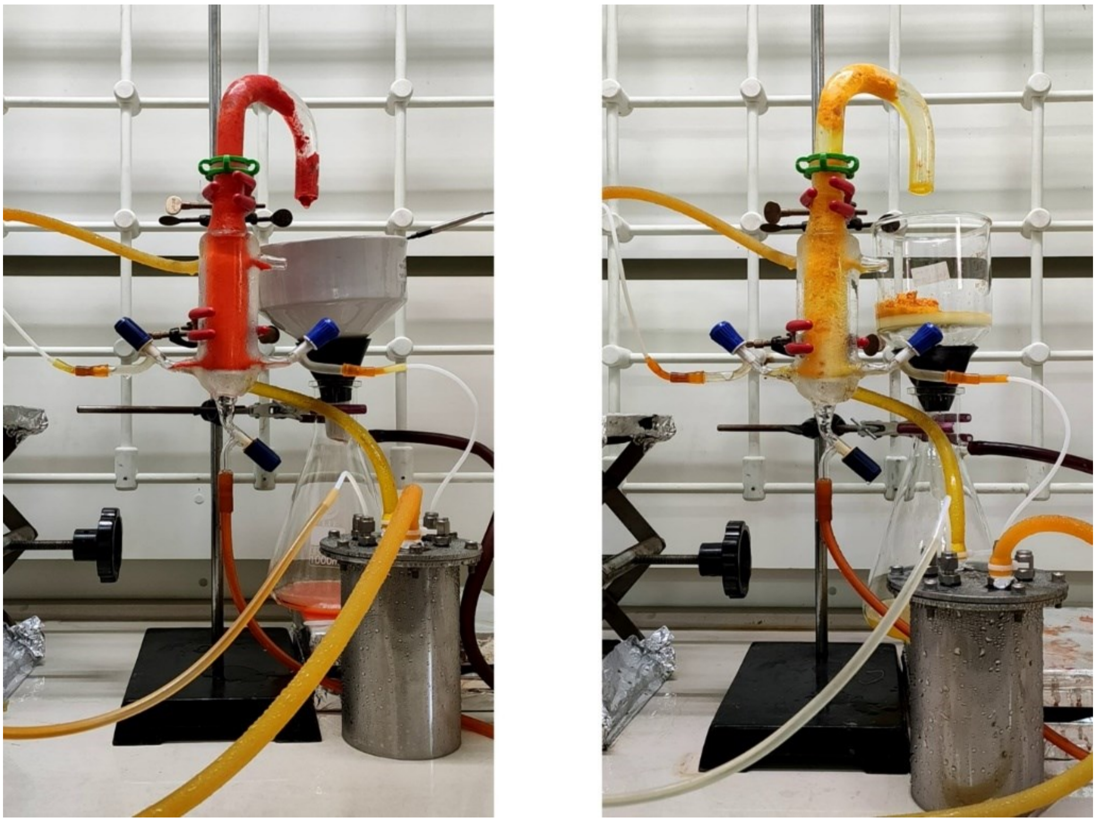


Figure 1S. Initial continuous flow step for azo dye synthesis



(a) (b)

Figure 2S: Modified setup with overhead flow for bubble column reactor for azo compound synthesis. (a) Sudan-I dye and (b) Solvent Yellow 16 dye

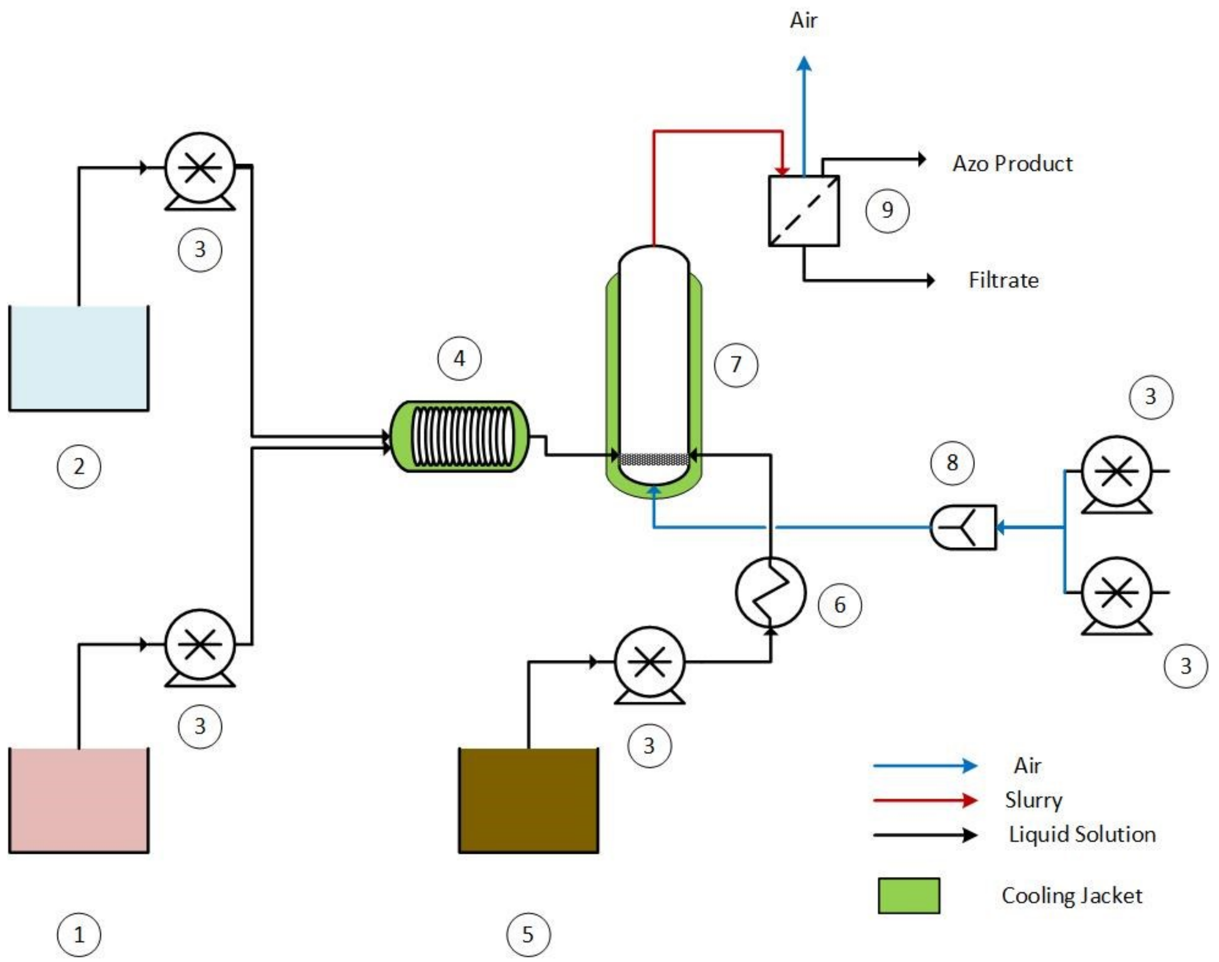
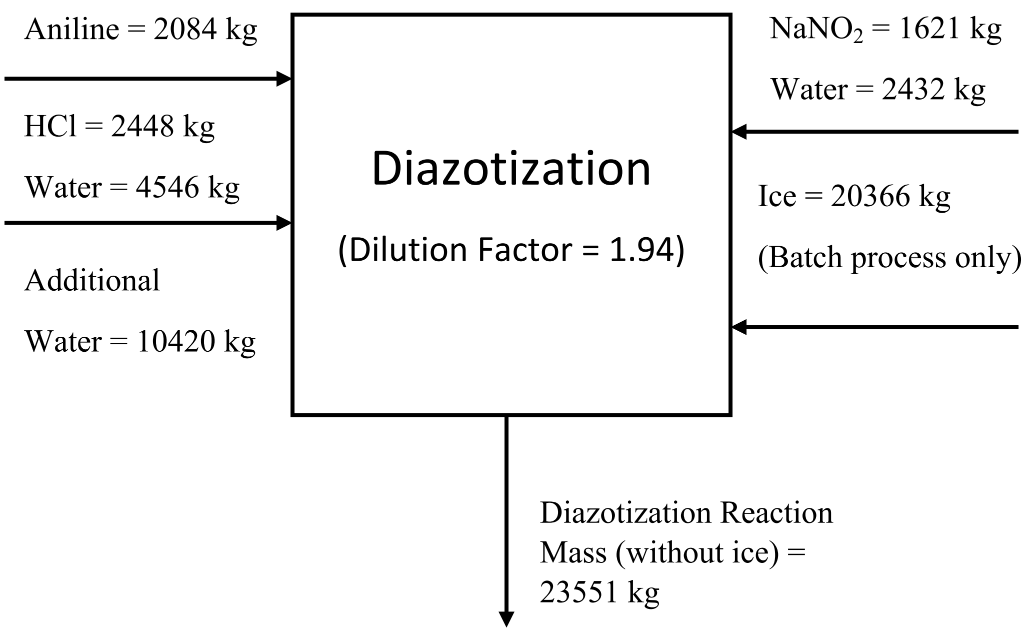


Figure 3S. Process flow diagram for the synthesis of azo dyes. (1) Pre-cooled solution of Aniline hydrochloride salt in water, (2) Pre-cooled solution of sodium nitrite, (3) peristaltic pumps, (4) Jacketed tubular reactor, 1/8 inch OD, 2 mm ID and 15 mL Teflon coil, (5) Pre-cooled Coupler + base solution, (6) Coiled Tubular heat exchanger, (7) Jacketed bubble column reactor, active volume 53 mL, (8) T-mixer and (9) Vacuum filtration assembly

S3. Calculation for Ice Water Needed for 5 TPD Sudan I Dye Plant (Batch Mode)

In order to do the techno-economic analysis, we consider a case study of 5 TPD Sudan I Dye plant. The main objective was to compare the continuous and batch plant sizes. It was assumed that the quantity of process water is the same for the batch and continuous process and the yield of azo dye with respect to aniline is 90% in both cases. Mass and energy balance was performed for both batch and continuous process. Based on the mass balance calculations, inlet temperature, and heat duty the quantity of required ice was calculated for the batch process. Ice after melting inside the reactor will increase the reactor volume and further dilute the reaction. Assumptions (heat capacity = 4.18 kJ/kg^{o}C, (− ΔH = 65 - 150 kJ/mol, inlet temperature/ambient temperature = 35 ^{o}C)

S3.1 Diazotization: Mass Balance for Ice (ΔH= -150 kJ/mol)



Diazotization Reaction Mass = 23551 kg

In a batch process ice is used to cool the reaction mass and also remove the heat of reaction during the reaction.

Heat duty for cooling reaction mass from 35 °C to 0 °C:

$Q = mC_p\Delta T$

$Q = 23551\ kg\ \times 4.18\ \frac{kJ}{kg°C} \times (35\ °C - 0\ °C) = 3445511\ kJ$

Mass of Ice required for cooling duty

$m_{c1} = \frac{Q}{L_f}$

$m_{c1} = \frac{3445511\ kJ}{334\ \frac{kJ}{kg}} = 10316\ kg$

Heat duty for removing heat of reaction

$Q_r = moles\ of\ aniline\ \times (- \Delta H)$

$Q_r = 22378\ mol\ \times 150\ \frac{kJ}{mol} = 3356700\ kJ$

Mass of Ice required for removing heat of reaction

$m_{c2} = \frac{Q_r}{L_f}$

$m_{c2} = \frac{3356700\ kJ}{334\ \frac{kJ}{kg}} = 10050\ kg$

Total ice required for diazotization

$m_c = m_{c1} + m_{c2}$

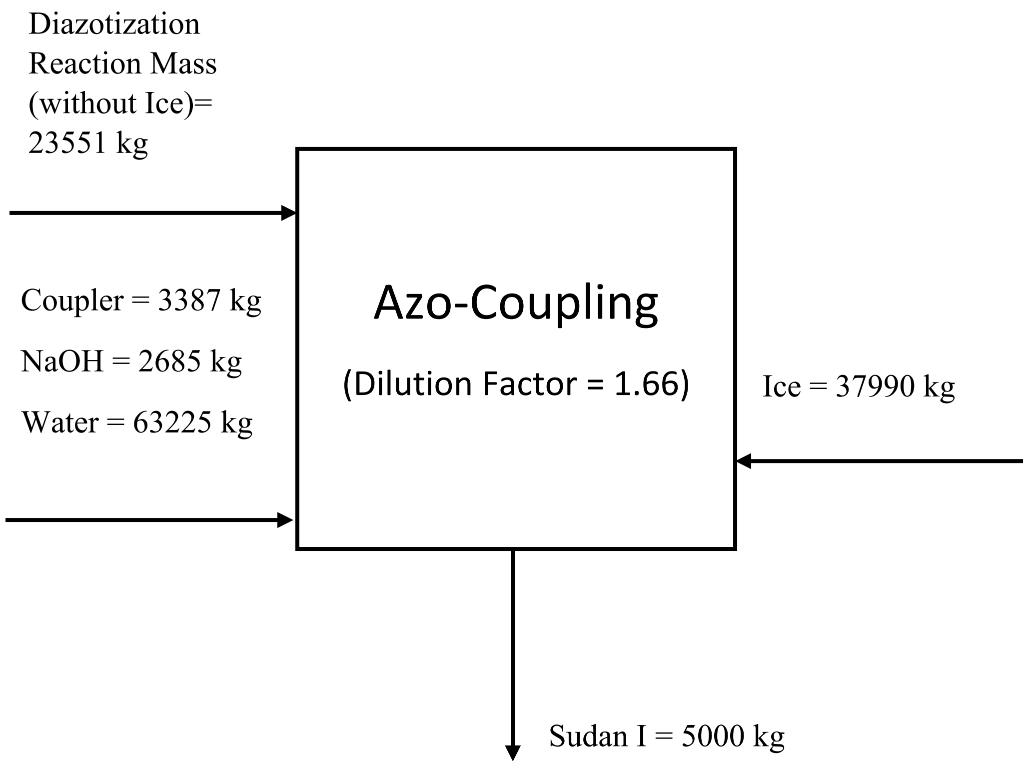
$m_c = 10316\ kg + 10050\ kg = 20366\ kg$

Total reaction volume before ice addition = 21580 L

Total reaction volume after ice addition = 41946 L

Dilution factor = 41946/21580 = 1.94

S3.2 Coupling Reaction: Mass Balance for Ice



Diazotization reaction mass (m_1) = 23551 kg at 0 ^{o}C

Total Coupler solution mass (m_2) = 69297 kg at 35 ^{o}C

Average temperature after mixing of diazonium solution and coupler solution

$$T_{avg} = \frac{m_1 C_p T_1 + m_2 C_p T_2}{m_1 C_p + m_2 C_p}$$

$$T_{avg} = \frac{\left(23551\ kg \times 4.18 \frac{kJ}{kg\ K} \times 273\ K\right) + \left(69297\ kg \times 4.18 \frac{kJ}{kg\ K} \times 308\ K\right)}{\left(23551\ kg \times 4.18 \frac{kJ}{kg\ K}\right) + \left(69297\ kg \times 4.18 \frac{kJ}{kg\ K}\right)}$$

$$T_{avg} = 299.12\ K = 26.12\ ℃$$

Heat duty required for cooling the coupler mass from 26.76 ^{o}C to 0 ^{o}C

$$Q = (m_1 + m_2) \times\ C_p \times \Delta T$$

$$Q = (23551\ + 69297\ )kg \times\ 4.18\ \frac{kJ}{kg\ ℃} \times 26.12\ ℃ = 10137293\ kJ$$

Mass of ice required for cooling the coupler mass,

$$m_{c3} = \frac{Q}{L_f}$$

$$m_{c3} = \frac{10137293\ kJ}{334\ \frac{kJ}{kg}} = 30352\ kg$$

Heat duty for removing heat of reaction for neutralization

$$Q_r = moles\ of\ HCl\ \times (- \Delta H)$$

$$Q_r = 44756\ mol\ \times 57\ \frac{kJ}{mol} = 2551092\ kJ$$

Mass of Ice required for removing heat of reaction

$$m_{c4} = \frac{Q_r}{L_f}$$

$$m_{c4} = \frac{2551092\ kJ}{334\ \frac{kJ}{kg}} = 7638\ kg$$

Total ice required for coupling reaction

$$m_c = m_{c3} + m_{c4}$$

$$m_c = 30352\ kg + 7638\ kg = 37990\ kg$$

Total ice for both reaction

$m_c = 20366\ kg + 37990\ kg = 58356\ kg$

Total volume of coupling reaction without ice = 88712 L

Total volume of coupling reaction with ice = 147070 L

Dilution factor = 147070 /88712 = 1.66

Water Reduction Scope

Table 1S. Comparison of water usage for batch and continuous process

	Batch	**Continuous**
Process Water (kg or L)	80623	80623
Ice for Cooling (kg)	58356	No ice required (cooling jacket/coil)
Total Water (kg or L)	138979	80623

Percentage Water Reduction $= \left(\frac{138979 - 80623}{138979}\right) \times 100 = 41.99\ \%$

If heat of reaction of coupling reaction and washing water is considered the percentage water reduction would increase further.

S4. Reactor Sizing and Design for 5 TPD Sudan I Dye Continuous Plant

Reactor Sizing for Tubular Reactor for Diazotization Reaction

The reactor volume was calculated based on the optimum residence time obtained at lab-scale and the total volumetric flowrate (for 5 TPD scale). In the case of the diazotization reactor, the diameter and length of the tubular reactor were estimated by iterative calculations such that the heat transfer area of the reactor is sufficient to remove the heat released during the reaction (heat of reaction (kJ/mol) multiplied by the molar flowrate (mol/s)). Gnielinski's correlation for heat transfer[2] was used to predict the heat transfer coefficient. Tube side heat transfer coefficient was considered the limiting factor to estimate the overall heat transfer coefficient (U_o). An iterative procedure was done in MS-Excel to find desired tube size which can provide the necessary heat transfer area and required volume. The iterative procedure is similar to heat exchanger design (assuming overall heat-transfer coefficient to calculate tube diameter (using equation 1S) and recalculate the actual overall heat transfer coefficient using correlations. The optimization solver was used to minimize the percent error between assumed and calculated overall heat transfer coefficient. The obtained tube diameter can be further used for calculating reactor length. The Tube OD/ID ratio was assumed as 1.625 and the log mean temperature difference (LMTD) was considered 10 ^oC. The below example shows the calculation for the heat of reaction = -150 kJ/mol. The solution was converged for U_o = 390.37 W/m^2K.

Reactor volume required = Residence time (min) × Total Flowrate (L/min) = 2 min × 14.98 L/min = 29.97 L = 0.02997 m^3

Heat Duty = Heat of reaction (-ΔH, kJ/mol) × molar flowrate (mol/s) = (150 kJ/mol × 15.54 mol/min) /60 = 38.85 kW

Reactor Volume

$$Reactor\ Volume = \frac{\pi d_i^2 L}{4} = 0.02997\ m^3$$

Required Heat Transfer Area

$$Required\ Heat\ Transfer\ Area = \frac{Heat\ Duty\ (kW) \times 1000}{Overall\ heat\ transfer\ coefficient\ \left(\frac{W}{m^2K}\right) \times LMTD\ (K)} = \frac{38.85 \times 1000}{390 \times 10} = 9.96\ m^2$$

Reactor Heat Transfer Area

$$Reactor\ Heat\ Transfer\ Area = \pi d_o L = 9.96\ m^2$$

Objective function for tube diameter optimization

$$\frac{Required\ Heat\ Transfer\ Area}{Required\ Reactor\ Volume} = \frac{\pi d_o L}{\frac{\pi d_i^2 L}{4}} = \frac{4 \times 1.625}{d_i} \qquad (1S)$$

Table 2S. Variable/Parameter values for the converged solution for tubular reactor for diazotization reaction

Variable/Parameter	**Value**	**Unit**
Cross-section area of reactor	0.000301	m^2
Fluid Velocity	0.83	m/s
Reynolds Number (Re)	9070	-
Prandtl Number	12.48	-

Nussalt Number	89.78	-
Fouling Factor, Glycol (utility)	0.00035	m^2K/W
Fouling Factor, water (reactor side)	0.000143	m^2K/W
Wall thermal resistance	0.0008876	m^2K/W
Overall heat transfer coefficient	390.37	W/m^2K
Reactor tube ID (di)	0.01957	m
Reactor tube length (L)	99.63	m

Reactor Sizing for Bubble Column Reactor for Azo Coupling

The uniformity of slurry and heat transfer coefficient largely depends on the superficial gas velocity.[3-5] Hence, a higher superficial gas velocity of 0.1 m/s was considered which can give churn turbulent regime.[3] Industrial bubble columns have an aspect ratio greater than 5,[6] and hence aspect ratio of 8 was considered. The gas hold-up was calculated using correlation by Smith et al[7] given by equation (2S-3S).[6-8] The heat transfer coefficient was calculated using Suh and Deckwer[9] correlation given by equation (4S-5S).[6, 9, 10]

$$\varepsilon_g = \left[2.25 + \left(\frac{0.379}{V_g}\right)\left(\frac{\rho_{sl}}{72}\right)^{0.31}\left(\mu_{sl}\right)^{0.016}\right]^{-1} \quad (2S)$$

$$\mu_{sl} = \mu_l \, exp\left[\frac{\left(\frac{5}{3}\right)v_s}{1 - v_s}\right] \quad (3S)$$

$$h = 0.1\left(k_l\rho_l C_{pl}\left\{\left[V_g\left(\varepsilon_s\rho_s + \varepsilon_l\rho_l + \varepsilon_g\rho_g\right)\right]g\left(\varepsilon_l\mu_b\right)^{-1}\right\}^{1/2}\right)^{1/2} \quad (4S)$$

$$\mu_b = \mu_l \, exp\left(\frac{2.5v_s}{1 - 0.609v_s}\right) \quad (5S)$$

For reactor sizing of bubble column reactor initially, the active volume was calculated using residence time of 4.5 min and volumetric flowrate based on 5 TPD Sudan I production scale. LMTD of 10 ^{o}C and heat of reaction of the neutralization reaction were considered. The required heat transfer was calculated and compared with the bubble column surface area. The additional heat transfer area can be provided by using an internal cooling coil (10.3 mm OD standard pipe). The required length and volume of the cooling coil were calculated and the actual volume of the reactor was calculated to estimate the diameter and height of the reactor. Table 3S shows the parameter values for the bubble column reactor.

Table 3S. Parameter values for the design of bubble column reactor for azo coupling

Variable/Parameter	**Value**	**Unit**
Inner Diameter (di)	0.38	m
Reactor Height	3.02	m
Aspect Ratio	8.0	-
Cooling coil OD	0.0103	m
Cooling coil length	364.7	m
Cooling coil volume	0.0304	m^3
Air Hold-up	9.87	%
Overall Heat Transfer Coefficient	194.78	W/m^2K
Total Reactor Volume	0.3379	m^3
Active Volume of bubble column reactor after inserting cooling coil	91.01	%

S5. Techno-Economic Analysis for 5 TPD Sudan I Dye Plant

Capital Cost Estimation

Reactor sizing was done using throughput, residence time calculations, and using correlations for design variables as discussed in the previous section. Further weight of the vessel/reactors was calculated using equation (6S). The standard thickness was considered based on the diameter range.[11, 12] The cost of the cylindrical shell was calculated based on material of construction (The cost of SS316 was considered as 6.57 \$/kg, while the cost of Hastelloy C276 was considered 5.4 times that of SS316). The cost of the bottom shell and fabrication was assumed as 20% each of the shell cost for storage tanks and batch reactors. The auxiliary cost (agitator and reactor supports) was assumed as 50% of the shell cost. For jacketed storage tanks the auxiliary cost (jacket, agitator and reactor supports) was assumed as 100% of the shell cost. For continuous tubular reactor the auxiliary cost (jacket and reactor supports) was assumed as 30% of the tube cost. For continuous bubble column reactor the auxiliary cost (jacket, support, cooling coil and sparger) was assumed as 200% of the shell cost. Tables T4S-T7S show the details for storage vessels and reactors for batch and continuous process. For the batch process, two pumps of 1398 L/min and 2238 L/min capacity are required for transferring the diazonium salt solution and coupler solution respectively into the coupling reactor (assuming 30 min transfer time). In the case of a continuous process, five pumps with a flow rate capacity of 1.4

L/min to 46.61 L/min are required. The cost of pumps, heat exchangers and air compressor were estimated using costing charts and cost indices.

$$W_t = 3.14 d_{avg} H t_s \rho \qquad (6S)$$

Table 4S. Reactor sizing and cost of batch vessels

Batch Process	Diazotization Tank	Coupler Solution Tank	Azo Coupling Tank
Average Diameter (m)	2.62	3.07	3.98
Height (m)	7.83	9.16	11.90
Vessel Thickness (m)	0.01	0.012	0.012
Weight of Shell (kg)	4966	8154	13742
Cost of Shell ($)	32626	53573	90286
Cost of Bottom Shell ($) (Assumed 20% of Shell cost)	6525	10715	18057
Cost of fabrication ($) (Assumed 20% of Shell cost)	6525	10715	18057
Cost of Auxiliary Equipment ($)[a]	16313	26786	45143
Total Cost ($)	61989	101789	171544

[a] Assumed 50% of the shell cost. Includes agitator and supports

Table 5S. Continuous feed storage tanks (aniline, HCl and water) sizing and cost

Continuous Feed Storage Tank	Aniline Tank	HCl (35%) Tank	Water Tank
Average Diameter (m)	0.66	0.95	1.14
Height (m)	1.98	2.83	3.41
Vessel Thickness (m)	0.005	0.005	0.007
Weight of Shell (kg)	158.8	325.4	661

Cost of Shell ($)	1043	2138	4349
Cost of Bottom Shell ($) (Assumed 20% of Shell cost)	209	427	870
Cost of fabrication ($) (Assumed 20% of Shell cost)	209	427	870
Cost of Auxiliary Equipment ($)[b]	104	214	435
Total Cost ($)	1565	3206	6524

[b] Assumed 10% of the shell cost. Includes vessel supports.

Table 6S. Continuous feed storage tanks (sodium nitrite and coupler) sizing and cost

Continuous Feed Storage Tank	**Sodium Nitrite Tank**	**Coupler Storage Tank**
Average Diameter (m)	0.77	2.13
Height (m)	2.3	6.35
Vessel Thickness (m)	0.005	0.009
Weight of Shell (kg)	214	2941
Cost of Shell ($)	1408	19323
Cost of Bottom Shell ($) (Assumed 20% of Shell cost)	282	3864
Cost of fabrication ($) (Assumed 20% of Shell cost)	282	3846
Cost of Auxiliary Equipment ($)	704[c]	19323[d]
Cost ($) per Unit	2676	46374
Number of Units	2	2
Total Cost ($)	5352	92748

[#]C1 Configuration: Tank refilled 3 times per day in cyclic manner
[c] Assumed 50% of shell cost. Includes agitator and supports
[d] Assumed 100% of shell cost. Includes jacket, agitator and supports.

Table 7S. Continuous reactor sizing and cost (Hastelloy C276 was used as MOC)

Continuous Reactors	**Tubular Reactor for Diazotization**	**Bubble Column Reactor for Azo Coupling**
Average Diameter (m)	0.025	0.38
Height or Length (m)	99.6	3.02
Vessel/Tube Thickness (m)	0.006	0.005
Weight of Shell (kg)	437.15	161.27
Cost of tube/Shell ($)	15509	5721
Cost of fabrication ($) (Assumed 20% of Shell cost)	3102	1144
Cost of Auxiliary Equipment ($)	4653[e]	11443[f]
Total Cost ($)	23264	18308

[e] Assumed 30% of the tubular reactor cost. Includes jacket and supports.
[f] Assumed 200% of the shell cost. Includes jacket, support, cooling coil and sparger.

Cost comparison of downstream process equipment

Cost comparison of the various downstream equipment's like filtration, spray drying, precipitation tanks, etc. can be done using Equation (7S)[11, 12]. The capacity ratio of the equipment (for batch and continuous) will be same as the volume (or volume processed per day) ratio for the batch and continuous process. Due to ice dilution, the batch to continuous volume ratio is 1.65 which results in 1.35 times higher capital cost.

$$Cost\ of\ equip.\ a = cost\ of\ equip.\ b \left(\frac{capacity\ of\ equip.\ a}{capacity\ of\ equip.\ b}\right)^{0.6} \qquad (7S)$$

$$\frac{Cost\ of\ equipment\ in\ batch}{Cost\ of\ equipment\ in\ continuous} = (1.65)^{0.6} = 1.35 \qquad (8S)$$

Operating Cost Estimation

Refrigeration Cost Calculation[12]

For calculating refrigeration cost, Coefficient of Performance (COP) was estimated using equation (9S). The refrigeration cycle was assumed 70% efficient. Electricity cost was assumed as 0.111 \$/kWh. Equations (10S) and (11S) were used for calculating the refrigeration cost.

$$COP = \frac{T_1}{(T_2 - T_1)} \qquad (9S)$$

$$Shaft\ Work\ Required = \frac{Cooling\ Duty}{COP} \qquad (10S)$$

$$Annual\ Cost = Shaft\ Work\ (W) \times Operating\ hours\ per\ year\ \left(\frac{h}{year}\right) \times Cost\ of \left(\frac{\$}{kWh}\right) \qquad (11S)$$

Power requirements for pumping fluids

The total energy required for pumping the fluid was calculated from using equation (12S). The pump efficiency was assumed as 70%. The power can further be used for estimation of annual electricity cost.

$$g\Delta z + \frac{\Delta P}{\rho} - \frac{\Delta P_f}{\rho} - W = 0 \qquad (12S)$$

$$Power = \frac{W \times m}{\eta} \qquad (13S)$$

S6. Nomenclature

C_{pl}	Heat capacity of liquid, J/kgK
d_{avg}	Average diameter, m
g	Acceleration due to gravity, m/s^2
H	Height of equipment, m
h	Heat transfer coefficient, W/m^2K
k_l	Thermal conductivity of liquid, W/mK
L_f	Latent heat of ice, kJ/kg
m	Mass of reaction, kg
m_c	Mass of ice, kg
ΔP	Difference in system pressures, Pa
ΔP_f	Pressure drop due to friction, Pa
Q	Heat removed during cooling, kJ
Q_r	Heat released during reaction, kJ
T	Temperature, K
t_s	Vessel wall thickness, m

U_o Overall heat transfer coefficient, W/m^{2}K

V_g Superficial gas velocity, m/s

W Work done by fluid, J/kg

W_t Weight or Mass, kg

Δz Difference in elevations, m

Greek Letters

ε_g Gas hold-up

ε_l Liquid hold-up

ε_s Solid hold-up

η Efficiency

μ_b Viscosity of slurry, kg/ms

μ_l Viscosity of liquid, kg/ms

μ_{sl} Viscosity of slurry, kg/ms

ν_s Solid volume fraction

ρ Desntiy, kg/m^3

ρ_g Gas desntiy, kg/m^3

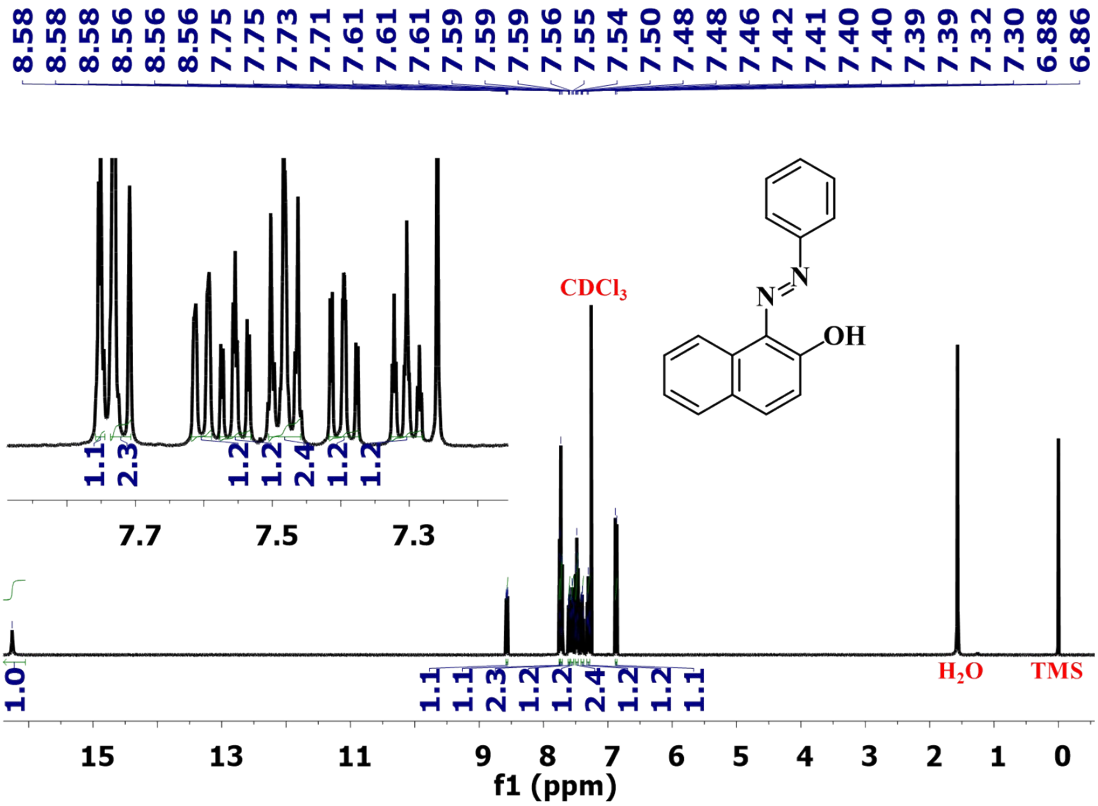
ρ_l Liquid desntiy, kg/m^3

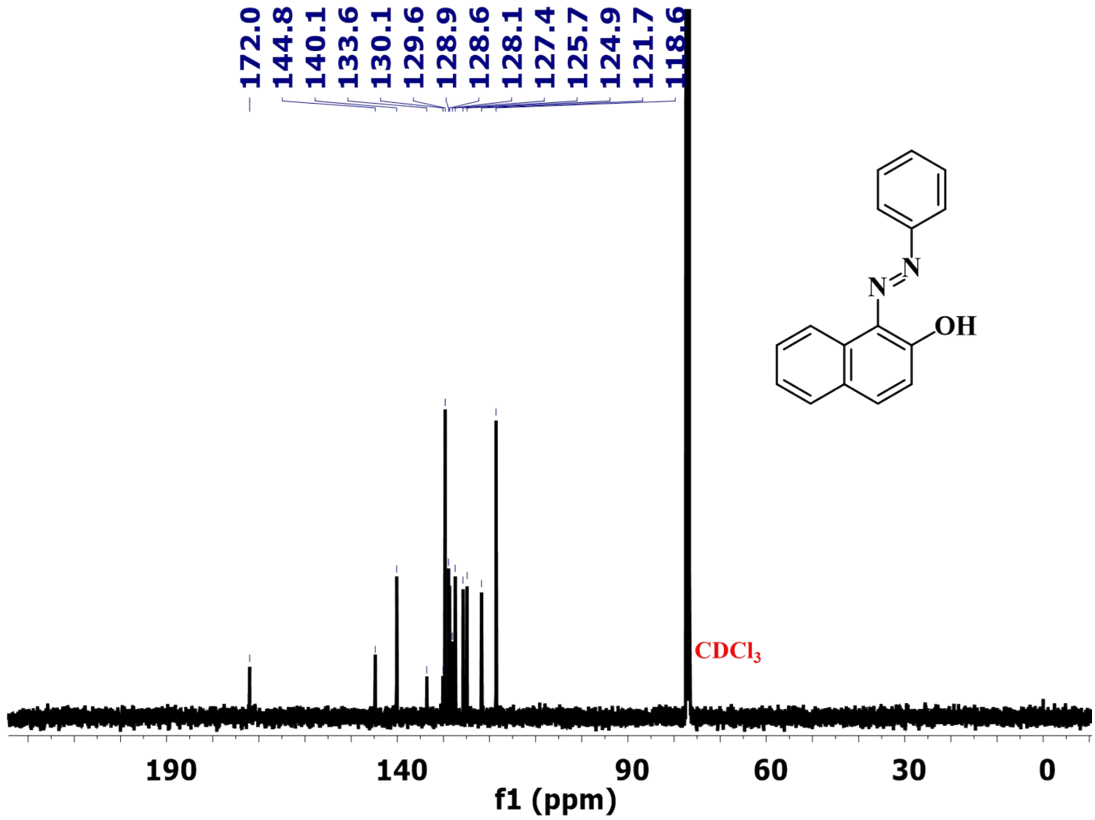
ρ_s Solid desntiy, kg/m^3

ρ_{sl} Slurry desntiy, kg/m^3

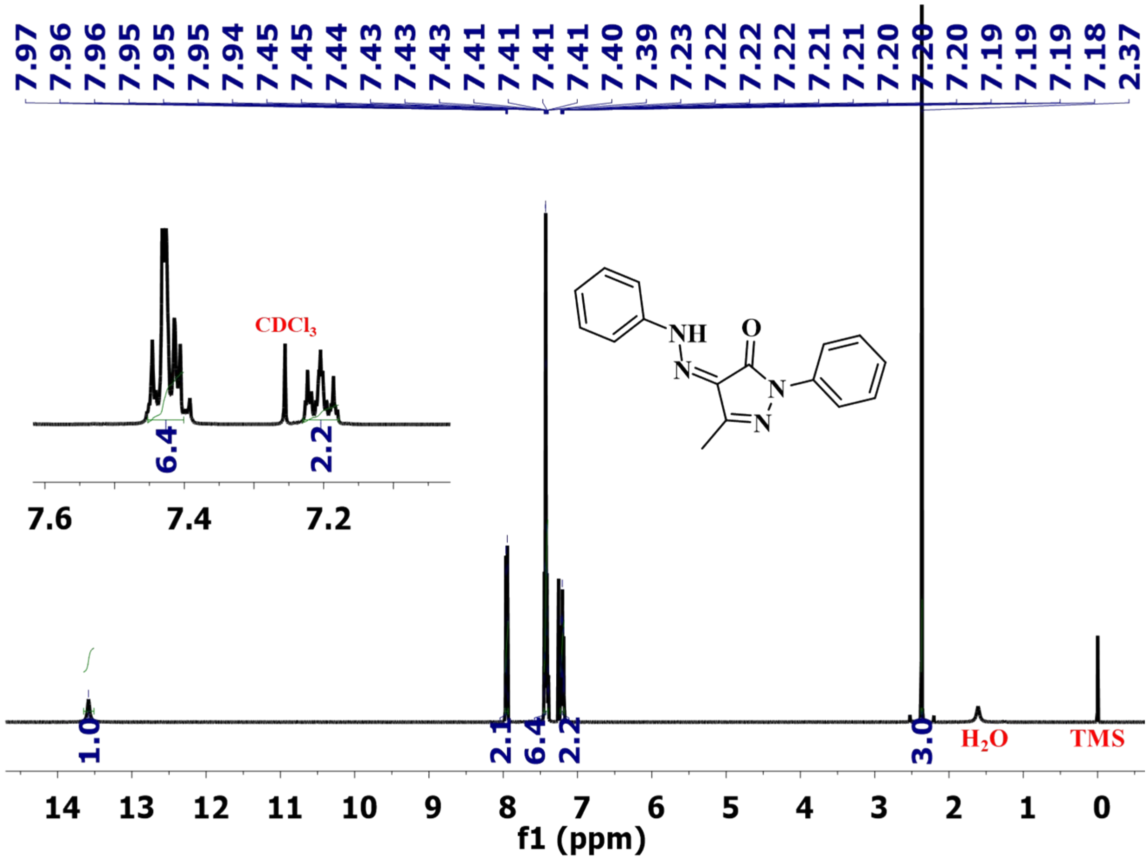
S6. NMR Spectra

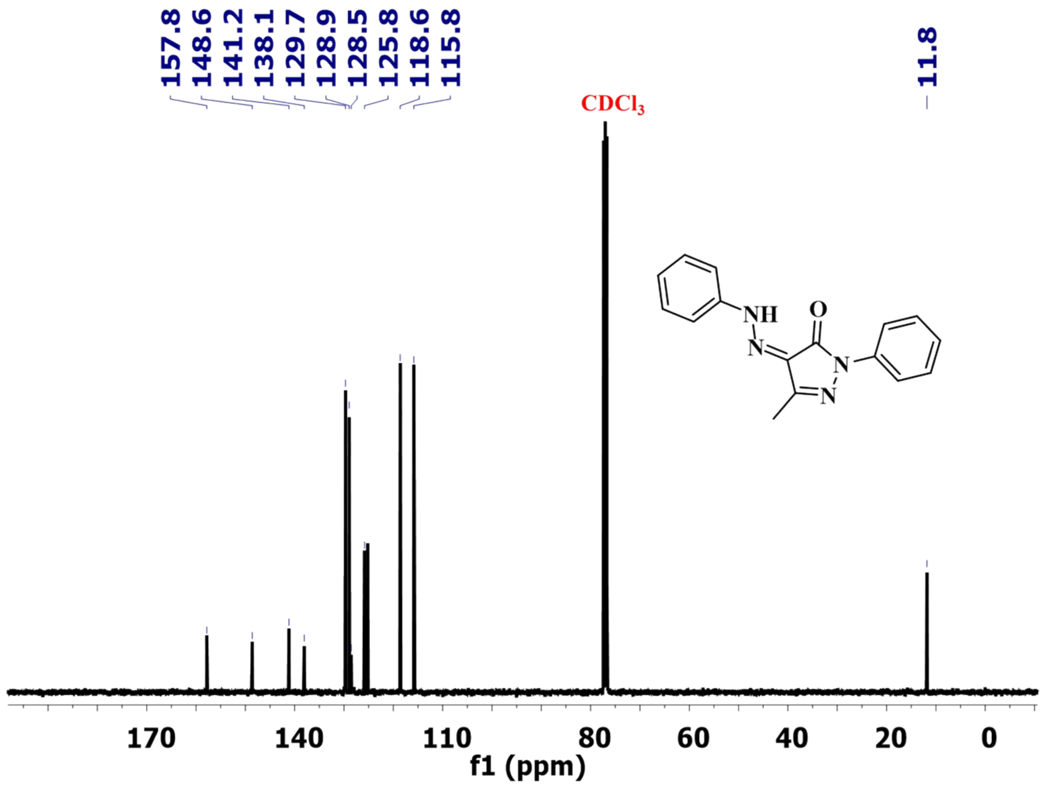
Sudan I Dye[1, 13]





Solvent Yellow 16[14]





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