# VisiMix Turbulent. Semi-Batch Nitration in Pilot Plant Reactor.

Subject of this example – application of the program VisiMix Turbulent for planning of pilot plant tests of nitration process.

## 1. Chemical and physical data.

Reaction equation:  $RH_2 + 2 HNO_3 > R (NO_2)_2 + 2 H_20.$ 

The pilot tests are planned as a next stage after laboratory research. Initial composition of nitrating acid (by weight):  $HNO_3 - 10\%$ ,  $H_2SO_4 - 75\%$ ,  $H_2O - 15\%$ .

Laboratory tests were performed in 1 liter glass reactor with mixer and jacket. Initial quantity of the nitrating acid - 0.8 kg. The organic reactant  $RH_2$  (85 g) was added during 5-10 min. Accordingly to the obtained results, at 55<sup>o</sup>C with 20-25% excess of nitrating acid practically 100% nitration is achieved.

**<u>Properties and constants</u>** – estimated values based on data and correlations of J.Perry's Chemical Engineers' Handbook.

#### Organic phase.

Initial product – RH2- liquid. Molecular mass – 130, Density – 1050 kg/cub.m, Viscosity – about 1 cP (at 55<sup>o</sup>C). Heat capacity – about 1400 J/(kg.K)

Final product – R(NO<sub>2</sub>)<sub>2</sub> - liquid Molecular mass – 174, Density – 1250 kg/cub.m, Viscosity – about 3 cP (at 55<sup>°</sup>C). Heat capacity – about 1700 J/(kg.K)

#### Nitrating acid.

#### Initial:

Density –1580 kg/cub.m, Viscosity – about 7 cP at 55<sup>0</sup>C. Heat capacity – about 1850 J/(kg.K). Heat conductivity – about 0.42 W/(m.K)

#### Final:

Density –1560 kg/cub.m, Viscosity – about 10 cP at 55<sup>0</sup>C. Heat capacity – about 1920 J/kg.

## Reaction heat release – 290 KJ/mol or 2250 KJ/ kg RH<sub>2</sub>.

# Characteristics of pilot reactor.

Tank with elliptical bottom, elliptical top and half-pipe coil. Main dimensions of tank and half-pipe coil are shown below.

TANK WITH ELI	IPTICAL BO	ттом			
Inside diameter	600	mm			
Total tank height	750	mm			
Total volume	197.9	I			750
Level of media	463.8	mm			
Volume of media	117	I	~	Ø 600	>
Figure 1.					

TANK SHELL CHARACTERISTICS					
Material	Stainless steel: AISI 316				
Wall thickness	4 mm 💌				
Thermal resistance of fouling	0.0002 (m²×K)/W				



Lower section			
Pipe diameter, lower section, d	80	mm	
Distance between coils, I	100	mm	l Pi
Number of starts	1		

TANK HEAT TRA	NSFER GEN	NERAL DAT	A			Help
Tank head type Jacket covers bottom Number of jacket sections Lower section	Elliptical YES 1					
Distance from bottom Height, Hlow Heat transfer area for	500	mm		+		
lower section If unknown, enter 0 *	I U	] sq.m		H low	d d	70000
Upper section					S S	R I
Distance between two sections		mm		-		
Height, Hup	[	mm				<u>~                                    </u>
Heat transfer area for					<del>≪</del> Ø 600	<del></del>



Figure 5.

# 2. <u>Ouantities of initial and final products.</u>

# Table 1.

Substances	Quantity		
	Kg-mol	kg	liter
Initial			
RH <sub>2</sub>	0.12	15.6	14.86
Nitrating acid,		185	117
Including HNO <sub>3</sub>	0.293	18.5	
H <sub>2</sub> O		27.8	
$H_2SO_4$		138,7	
Final			
$R(NO_2)_2$	0.12	20.88	16.7
Nitrating acid,		174.2	111.6
Including HNO <sub>3</sub>	0.053	3.35	
H <sub>2</sub> O		32.1	
$H_2SO_4$		138,7	

# 3. Outlined order of operation of the pilot reactor.

- Total quantity of nitrating acid is loaded into reactor.
- Cooling of the reactor is started.
- The RH2 is added by small quantities. The rate of adding is selected so as to increase the temperature to  $55^{0}$ C.
- The adding rate is decreased, it is controlled so as to keep the permanent temperature  $55^{\circ}$ C till the end of the process.

### 4. Applicability of mixing device.

#### 4.1. Liquid-liquid mixing.

The process consists in mass transfer between two immiscible liquids. So, the minimum requirement to mixing device – to ensure complete emulsification of disperse phase (organic) and exclude separation of phases on all stages of the process (see figure below).

Liquid-solid mixing	•	
Liquid-liquid mixing	Þ	KINETICS OF DROP BREAK-UP
Gas dispersion and mass transfer	►	Complete/incomplete emulsification
Liquid-solid mass transfer	►	Mean drop size Sauter mean drop size
Heat Transfer. Continuous flow (CF)	Þ	Specific mass transfer area
Heat Transfer. Batch (BH)	Þ	DISTRIBUTION OF DROPS BY DIAMETER Mean micromixing time inside drop
Heat Transfer. Semibatch (SB)	Þ	Micromixing time for disperse phase
Heat Transfer. Fixed temperature regime (FT)	Þ	Frequency of coalescence

Figure 6.

The input tables for the final state are shown below:

AVERAGE PROPERTIES OF MEDIA					
Type of media	Behavior of Non-Newtonian media is approximated with the functions:				
Average 1510 kg/cub.m 💌					
Dynamic viscosity 14 cP 💌	$\tau = \tau_0 + K * \gamma^n$				
Kinematic viscosity 9.272e-06 sq.m/s 💌	$\mu = \tau_{o} * \gamma^{-1} + K * \gamma^{n-1} ,$				

Figure 7.

PROPERTIES OF CONTINUOUS AND DISPERSE LIQUID PHASES.					
Continuous phase   Density   1560   kg/cub.m   Dynamic viscosity   10	Interfacial surface tension 0.025 N/m 💌				
Disperse phase Volume fraction 0.162 Density 1250 kg/cub.m Dynamic viscosity 3 cP	Index of admixtures 0.25 -10.5 - coagulants (de-emulsifiers) -0.50.1 - 2- and 3-valent ions of electrolytes -0.1 - 0.1 - no significant admixtures (pure oil - water) 0.1 - 0.25 - electrolytes 0.25 - 0.5 - small quantities of detergents 0.5 - 1 - detergents, emulsifiers				

Figure 8.



Figure 9.

SAUTER MEAN DROP SIZE				
Parameter name	Units	Value		
Sauter mean drop size	m	0.000156		



## **4.2. Checking the mixing power.** The power is much lower than power of drive – see below.

MIXING POWE	R	
Parameter name	Units	Value
Mixing power	W	175



#### 5. Temperature regime and production rate of pilot reactor.

Accordingly to the described order of operation, nitration in the pilot reactor is considered as a Semi-Batch process with significant heat release. The maximum process rate in the reactor is limited by cooling.

The process consists of two periods – initial period with increase of temperature to  $55^{0}$  C due to reaction heat and stable state period with constant temperature. Initial temperature in the reactor before nitration is assumed to be  $35^{0}$ C. Input tables for properties of reaction media and liquid cooling agent are presented below.

HEATING / COOLING LIQUID AGENT IN JACKET.				
Heating/cooling agent	Water	•		
Inlet temperature	20 °C	•		
Flow rate of heat transfer agent in lower jacket	1 cub.m/h	•		

Figure 12.

	HEAT TRANSFER PROF	ERTIES OF THE MEDIA	
Media	Water solution	•	
	PARAMETER	TI	EMPERATURE
Average density	1580 kg/cub.i	n 🔽 !	55 °C 💌
Dynamic viscosity	7 cP		55 °C 💌
Specific heat	1850 J/(kg*K)		55 °C 💌
Heat conductivity	0.42 W/(m*K)	•	55 °C 💌

Figure 13.

# 5.1. Semi-batch heat transfer. Stage 1 – heating period.

Purpose of calculation for this stage was defined as follows: to estimate fraction of  $RH_2$  that has to be introduced into reactor in order to increase temperature to  $55^{\circ}C$  within 10-15 min.

VisiMix modeling has been performed for injection from 0.1 to 0.5 of the total quantity of  $RH_2$ . Accordingly to the data of par.2 and 4, adding of total quantity of  $RH_2$  results in increase of volume of media by 11.3 liter. The total heat release is

 $0.12*1000*292000 = 3.5*10^7$  J.

Values of final volume and heat release for entering into the corresponding VisiMix input table are defined going out of this equation (Table 2).

### Table 2.

Fraction of total RH <sub>2</sub> quantity	Increase of volume, liters	Data for VisiMix i Final volume of media, liters	input table Heat release, J	VisiMix result - Final temperature of media, <sup>0</sup> C
0.1	1.13	118.13	$3.5*10^{6}$	35.4
0.2	2.26	119.26	7*10 <sup>°</sup>	42.4
0.3	3.39	120.39	$10.5*10^{6}$	49
0.4	4.52	121.52	$14*10^{6}$	54
0.5	5.65	122.65	$17.5*10^{6}$	60

Accordingly to the data of Table 2, one of the possibilities to satisfy requirements to the heating stage is to introduce about 40% (6.25 kg) of  $RH_2$  during the first 12 min. The corresponding input table and modeling results are presented below.







## 5.2. Semi-batch heat transfer. Stage 2 – period of constant temperature.

On the second stage 60% of the  $RH_2$  - about 9.4 kg- have to be added at constant temperature. The total heat release on this stage is

 $0.6*3.5*10^7 = 2.1*10^7$  J.

Heat transfer rate from the reaction media to cooling agent can be evaluated using VisiMix option **Heat transfer. Fixed temperature regime**. The corresponding input table and calculation results are presented below.



Figure 16.

HEAT TRANSFER RATE. FT. LA.					
Parameter name	Units	Value			
Heat transfer rate. FT.	W	12500			

Figure 17.

The RH<sub>2</sub> injection rate is:

# 12.5 KW / 2250 KJ/ kg = 0.0055 kg/s.

For 9.4 kg the injection time is about 1700 sec.

For a final evaluation, this stage is simulated as **Semi-batch heat transfer** with initial data accordingly to the input table below.

	SEMIBATCH	PROCESS.	HEAT	TRANSFER SPEC	IFIC DATA.		
Initial temperature in the tank	54	]°C	•	Final volume of media	128.3	1	•
Temperature of inlet flow	20	°C	•	Duration of reactants inlet	1700	s	-
Initial concentration of reactant A in the tank		mol/liter		Density of inlet flow	1050	kg/cub.m	•
Initial concentration of reactant B in the tank.		mol/liter		Specific heat of inlet flow	1400	J/(kg*K)	•
Concentration of reactant A in the inlet flow		mol/liter		Heat release (consumption) for a batch	2.1e+07	J	•
Concentration of reactant B in the inlet flow		mol/liter		Simulation time	2400	\$	•





Figure 19.

# 6. Evaluation of mass transfer in the reactor.

The calculations above are based on assumption of a relatively high reaction rate and efficient mass transfer.

In the current example the mass transfer in a batch or semi-batch reactor can be evaluated using the parameter **Mean micro-mixing time inside drop**. This parameter characterizes rate of mixing inside droplets. For 'fast' reactions it gives the maximum estimation of reaction time after formation of droplets. Evaluation of the time of formation is based on **Kinetics of drop break-up**.

Results of calculations for the input data shown in Figure 8 are shown below.

Accordingly to these results, drop formation and micro-mixing in the reactor is practically finished within 1.5 - 2 minutes after RH<sub>2</sub> injection - period short enough as compared to total batch duration. So, mass transfer limitation of the reaction is not probable.

MEAN MICROMIXING TIME INSIDE DROP				
Parameter name	Units	Value		
Mean micromixing time inside drop	s	24.4		







# 7. Scaling-up.

It follows from the data above that one of the main problems in development of a production scale process will be connected with heat transfer from the reaction media. For reproduction of mass transfer conditions, the values of Mean micro-mixing time inside drop and time of drop formation have to be reproduced.

# Conclusions.

- 1. Intensity of mixing in the pilot reactor is high enough to provide complete emulsifying of disperse phase (RH<sub>2</sub> and R(NO<sub>2</sub>)<sub>2</sub>) and relatively small mean drop sizes.
- 2. Nitration can be provided as a semi-batch operation, total nitration time for synthesis of 21 kg of product will be about 45 min or more.
- 3. Rate of nitration is limited by rate of cooling. Mass transfer rate in the reactor is relatively high, mass transfer limitation of the process rate is not expected.