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_20 –
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 55^0C with 20-25% excess of nitrating acid practically 100% nitration is achieved.

Properties and constants – 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 55^0C).
Heat capacity – about 1400 J/(kg.K)

Final product – $R(NO_2)_2$ - liquid
Molecular mass – 174,
Density – 1250 kg/cub.m, Viscosity – about 3 cP (at 55^0C). Heat capacity – about 1700 J/(kg.K)

Nitrating acid.

Initial:

Density –1580 kg/cub.m,
Viscosity – about 7 cP at 55^0C.
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 55^0C.
Heat capacity – about 1920 J/kg.

Reaction heat release – 290 KJ/mol or 2250 KJ/ kg RH_2.

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.

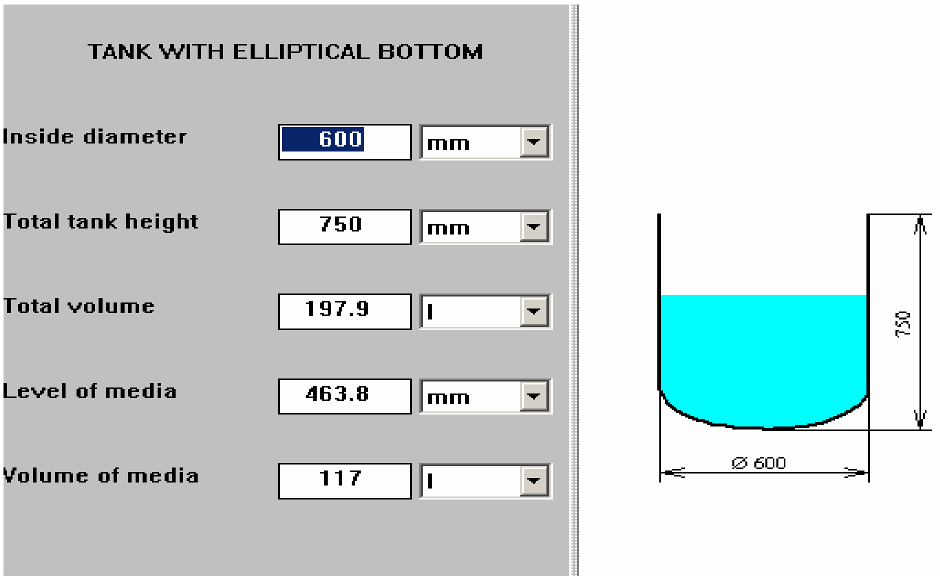


Figure 1.

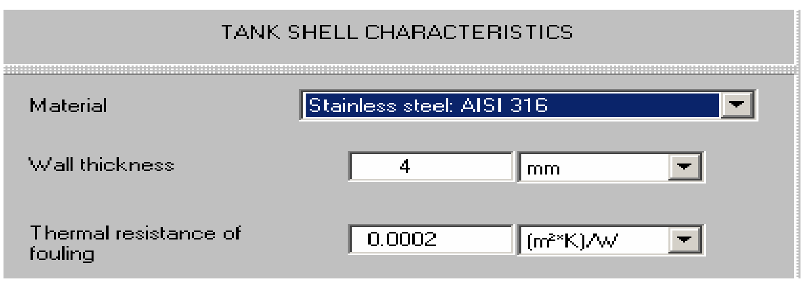


Figure 2.

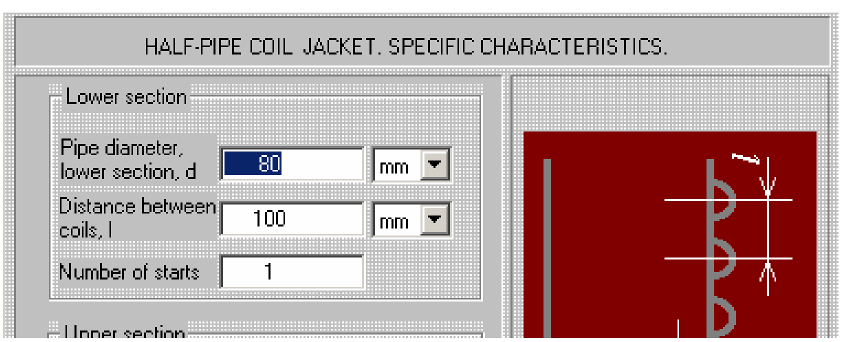


Figure 3.

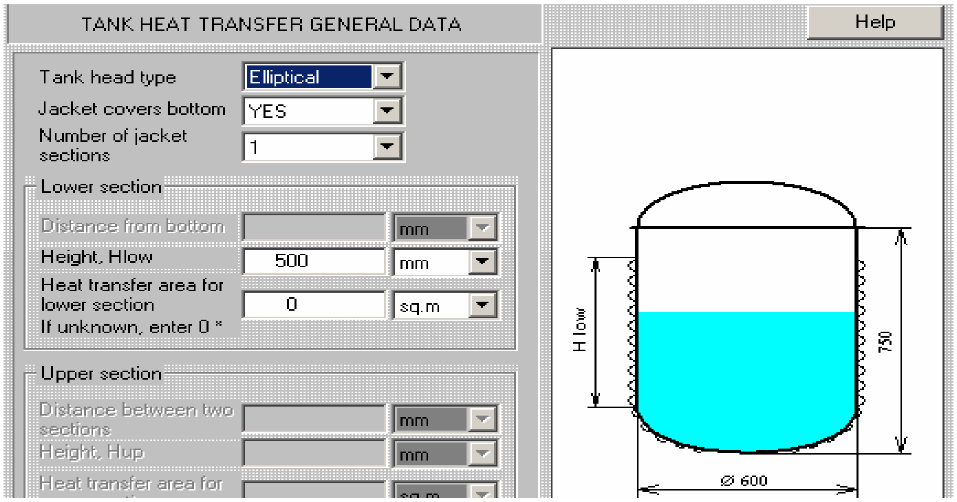


Figure 4.

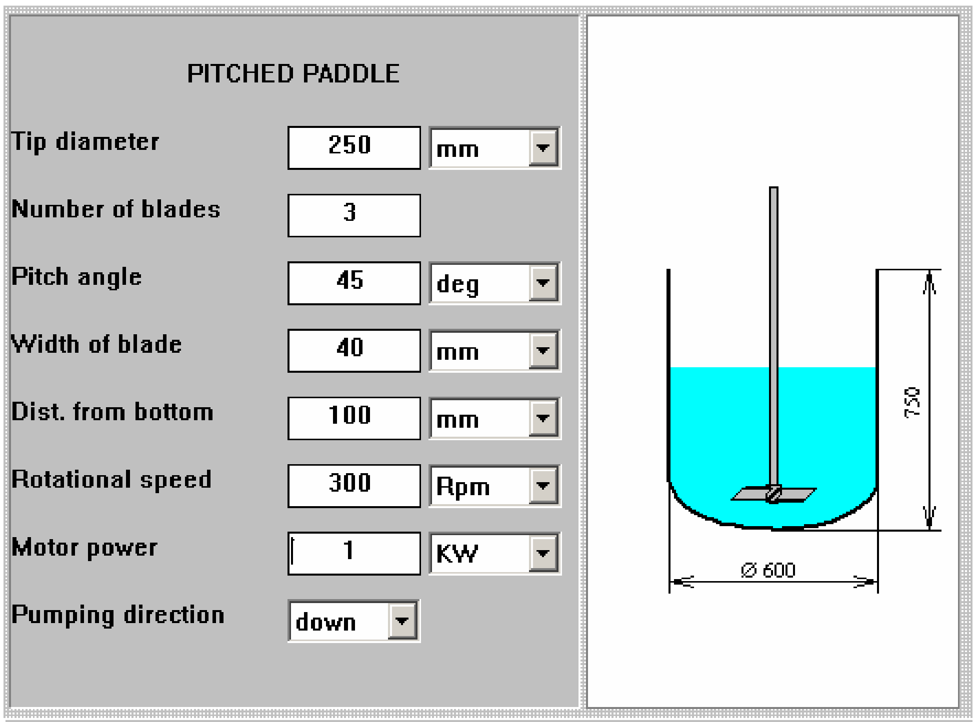


Figure 5.

2. Quantities of initial and final products.

Table 1.

Substances	Quantity		
	Kg-mol	kg	liter
Initial			
RH_2	0.12	15.6	14.86
Nitrating acid,		185	117
Including HNO_3	0.293	18.5	
H_2O		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_3	0.053	3.35	
H_2O		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 55^0C.
- The adding rate is decreased, it is controlled so as to keep the permanent temperature 55^0C 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).

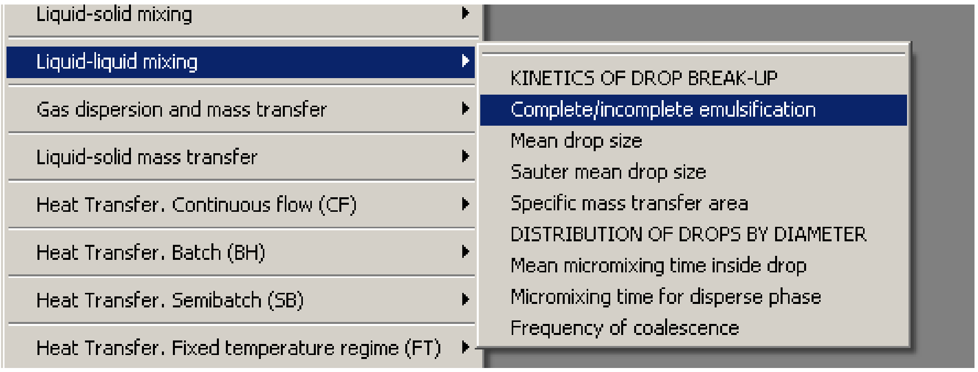


Figure 6.

The input tables for the final state are shown below:

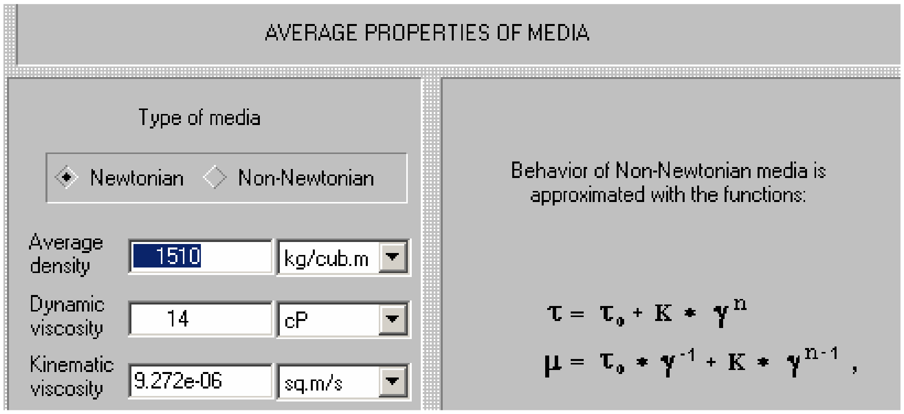


Figure 7.

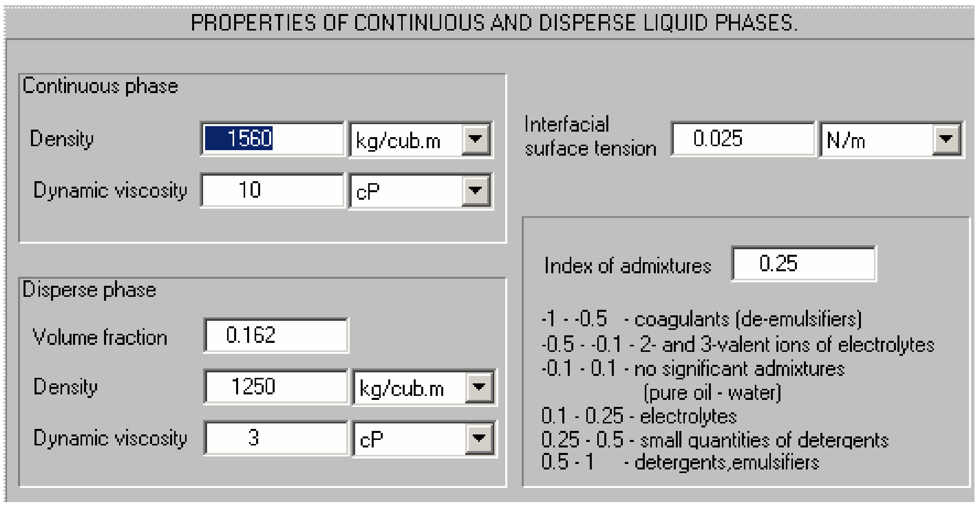


Figure 8.

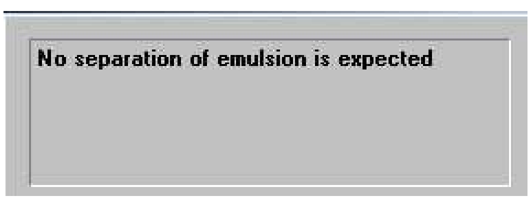


Figure 9.

SAUTER MEAN DROP SIZE

Parameter name	Units	Value
Sauter mean drop size	m	0.000156

Figure 10.

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

MIXING POWER

Parameter name	Units	Value
Mixing power	W	175

Figure 11.

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 35^0C. Input tables for properties of reaction media and liquid cooling agent are presented below.

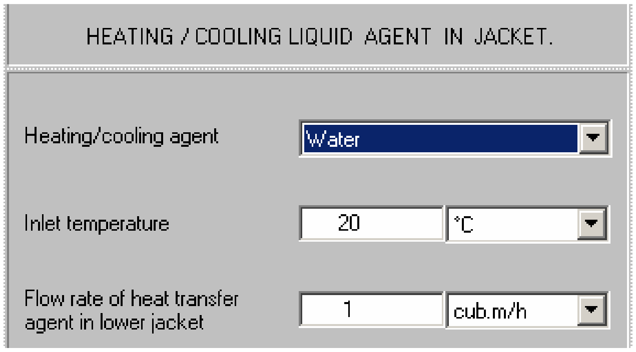


Figure 12.

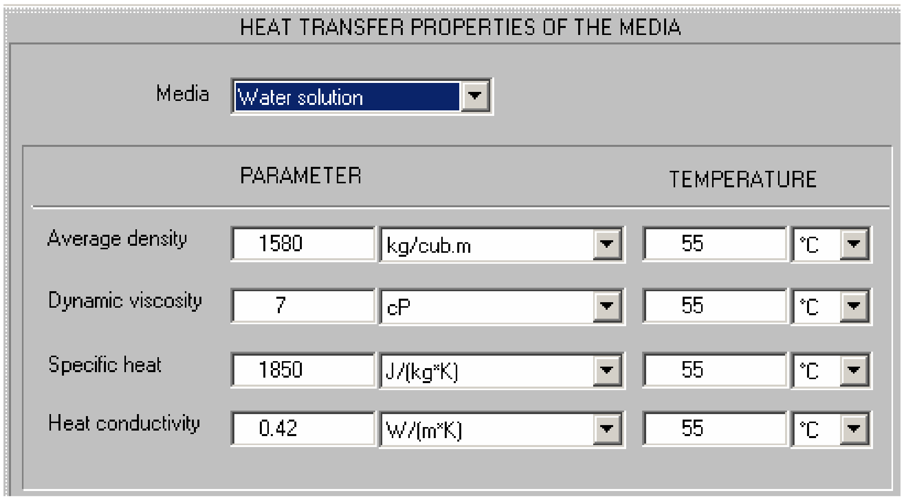


Figure 13.

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 55^0C 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_2 quantity	Increase of volume, liters	Data for VisiMix input table		VisiMix result - Final temperature of media, ^0C
		Final volume of media, liters	Heat release, J	
0.1	1.13	118.13	$3.5*10^6$	35.4
0.2	2.26	119.26	$7*10^6$	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.

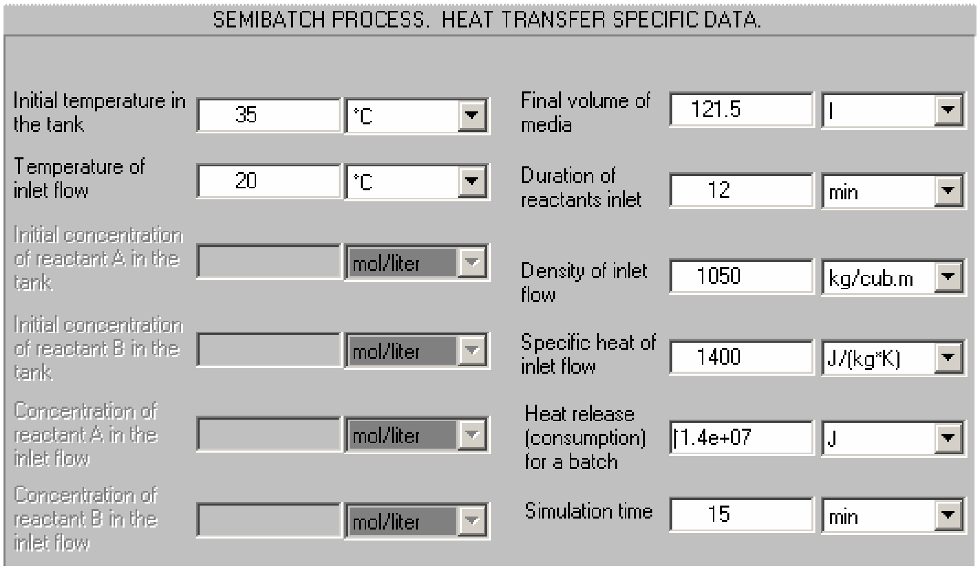


Figure 14.

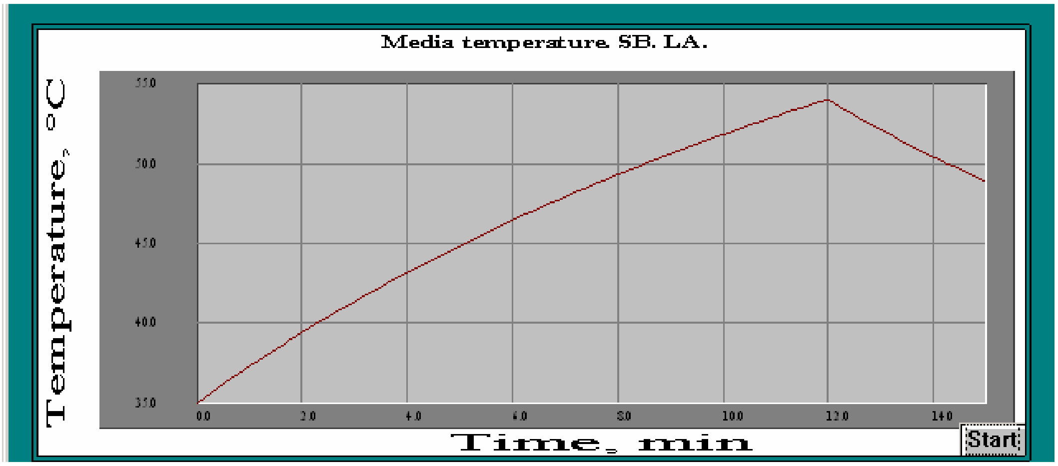


Figure 15.

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.

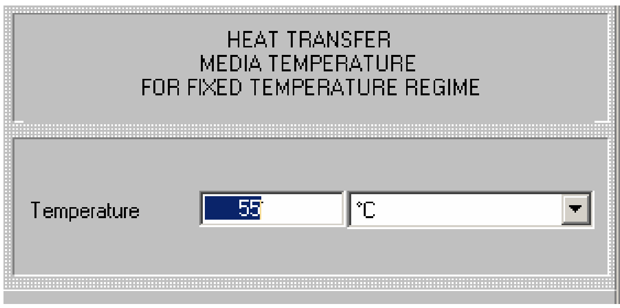
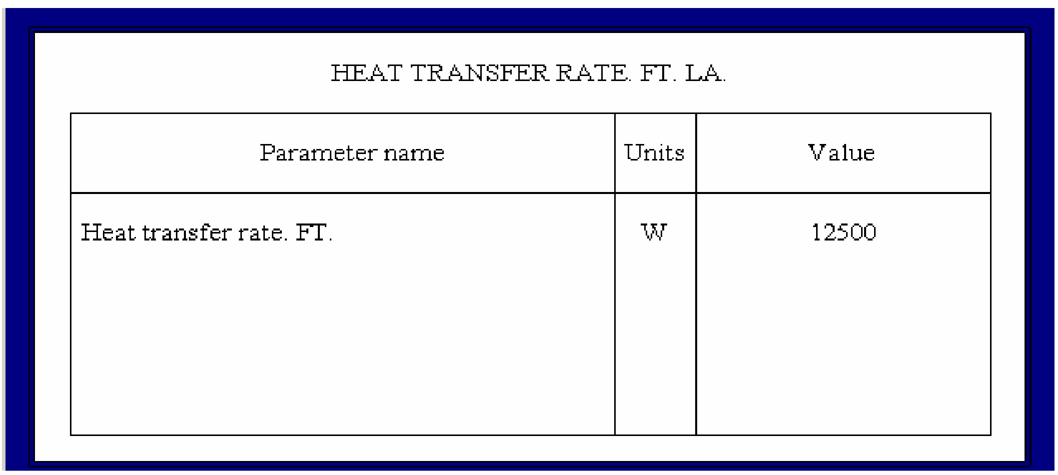


Figure 16.


HEAT TRANSFER RATE. FT. LA.

Parameter name	Units	Value
Heat transfer rate. FT.	W	12500

Figure 17.

The RH_2 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.

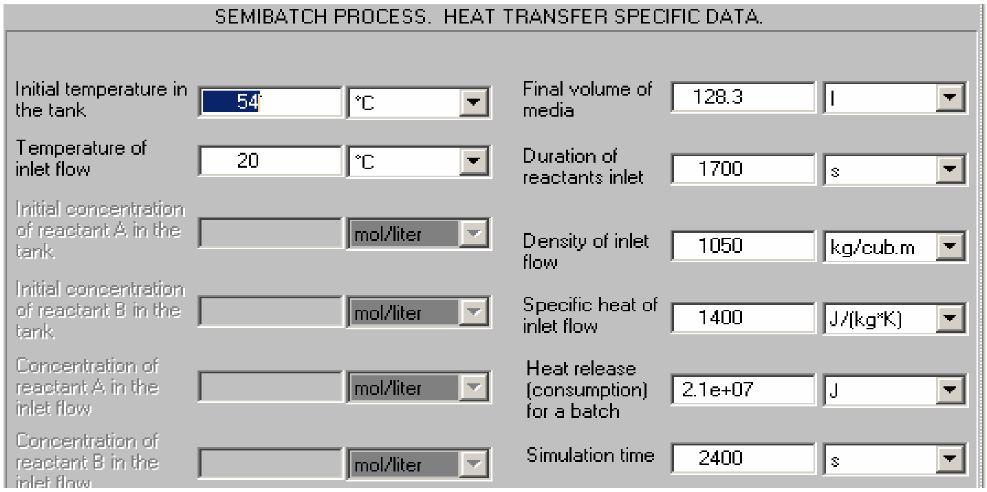


Figure 18.

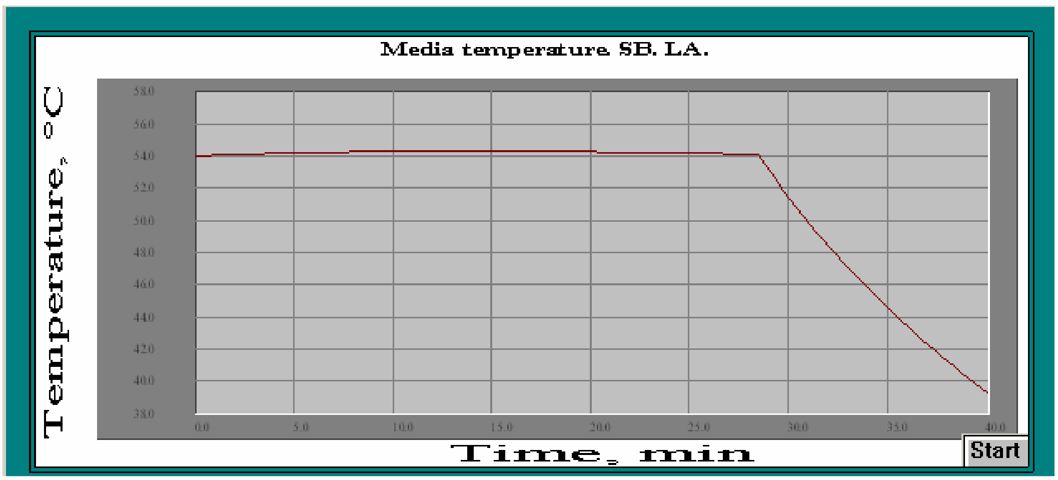


Figure 19.

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_2 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

For HELP press F1

Figure 20.

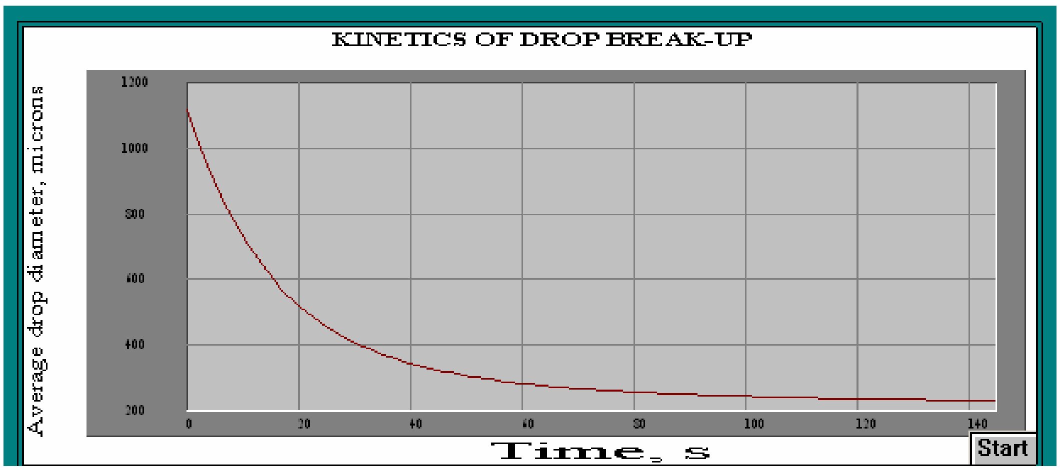


Figure 21.

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_2 and $R(NO_2)_2$) 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.