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Generalized net model of sulfuric acid manufacture from waste sulfuric acid

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Abstract

Generalized Nets (GN) have been used for the construction of a model, describing the process of sulfuric acid manufacture from waste sulfuric acid.

1. Introduction

In modern chemical industry, sulfuric acid is used as a reagent and catalyst. In petrochemical industry sulfuric acid finds application as catalyst and as a result of this considerable quantities of waste sulfuric acid, containing organic impurities is obtained. Utilization of waste sulfuric acid is of great ecological importance and allows its multiple reuse [1,2]. In Bulgaria, sulfuric acid is manufactures from pyrites and sulfur - containing gas from non-ferrous metallurgy. Sulfuric acid is used as a catalyst in manufacture "Sulfuric acid alkylation". Waste sulfuric acid obtained is polluted with organic impurities. It regeneration comprises thermic decomposition. This process coupled with energy expenses. The goal of the article is the construction of a model of production of sulfuric acid from waste sulfuric acid with Generalized Nets [3,4]. GNs suggest a powerful tool base for modelling of parallel, real-time flowing processes. They allow their simulation and the following of their behaviour in the future, their management and optimization.

2. Description of the process

Fig.1. shows the components and flows for the production of sulfuric acid from waste sulfuric acid. As initial raw material for sulfuric acid manufacture, waste solution of sulfuric acid from the manufacture "Sulfuric acid alkylation", containing (wt %): H_2SO_4 - 84, C - 4.4; H - 0.44, O - 0.61; S - 0.05; H_2O - 8.50, alkylsulfates - 2.0 is used. The residual solution is subjected to thermal decomposition following the reaction:

$$\mathbf{H_2SO_4 + C_nH_m + (n+0.25m-0.5)O_2 \rightarrow SO_2 + nCO_2 + (0.5\ m + 1)\ H_2O}$$

The process is endothermic and it is compensated through burning of hydrosulfuric gas, which is both fuel and sulfur containing raw material. The reaction is performed in an oven for decomposition of the sulfuric acid at 900 - 1200 ^oC. The oven gas passes through gas-pipe and heat exchanger 1 for cooling and after that enters the compartment for purification from mechanical impurities, predominantly sulfates and absorption of sulfur trioxid. The obtained wet gas is dried with 98 % sulfuric acid from the monohydrate absorber in a drying tower. The oxidation of the sulfur dioxide to sulfur trioxide is performed in a five layer converter with intermediate cooling in the presence of catalyst vanadium contacting mass. The heat of the oxidation reaction of sulfur dioxide to sulfur trioxide is used for heating the incoming for contacting gas in the heat exchangers 2-5.

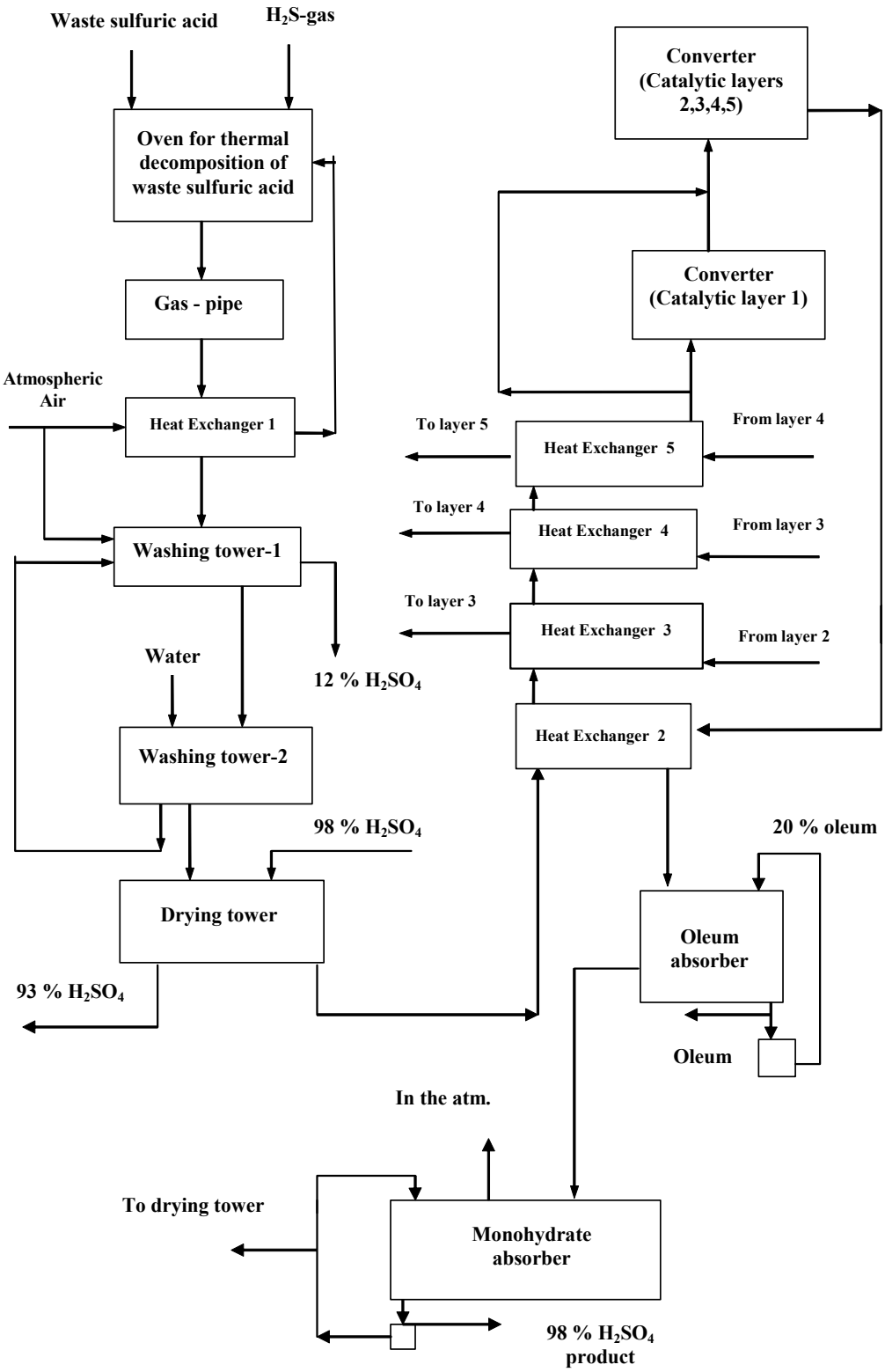

Fig.1. Components and flows for the production of sulfuric acid from waste sulfuric acid

The gas containing sulfur trioxide subsequently passes through oleum, and monohydrate absorbers resulting in concentrated 98 % sulfuric acid. After the absorption process, the obtained oleum and monohydrate sulfuric acid in cooled in sprayed cooling devices with water.

As final products, 98 % sulfuric acid is obtained. The obtained intermediate solutions of sulfuric acid with different concentrations (12 % H_2SO_4 from the washing tower, 93 % H_2SO_4 from the drying tower and oleum from the oleum absorber) are stored in tanks. They are used for adjustment the concentration of sulfuric acid and oleum in the washing tower, the drying tower, the monohydrate and the oleum absorbers.

3. A GN-model

Figure 2 shows the generalized net model, describing the process of production of sulfuric acid from waste sulfuric acid.

The generalized net contains the following set of transitions:

$$A= \{ Z_1, Z_2, Z_3, Z_4, Z_5 , Z_6, Z_7, Z_8 , Z_9, Z_{10}, Z_{11}, Z_{12} , Z_{13}, Z_{14}, Z_{15}, Z_{16}, Z_{17}, Z_{18}\},$$

where the transitions describe:

- The functions of the Oven for thermal decomposition of waste sulfuric acid – transition Z_1;
- The functions of the Gas pipe – transition Z_2;
- The functions of the Separator of the air, Separator of the sulfuric acid 98% and Separator of the oven gas – transitions Z_3, Z_{11} and Z_{15};
- The functions of the Heat Exchanger 1, Heat Exchanger 2, Heat Exchanger 3, Heat Exchanger 4 and Heat Exchanger 5 – transitions Z_4, Z_8, Z_{12}, Z_{13} and Z_{14};
- The functions of the Washing tower-1 and Washing tower-2 – transitions Z_5 and Z_6;
- The functions of the Drying tower – transition Z_7;
- The functions of the Oleum absorber – transition Z_9;
- The functions of the Monohydrate absorber – transition Z_{10};
- The functions of the Converter (Catalytic layer 1) and Converter (Catalytic layers 2, 3, 4, 5) – transitions Z_{16} and Z_{18};
- The functions of the mixer– transition Z_{17}.

Initially the GN contains the following tokens:

- β_4-token in place l_4 with characteristic “Oven for thermal decomposition of waste sulfuric acid”,
- β_6-token in place l_6 with characteristic “Gas-pipe”,
- β_{10}, β_{37}, β_{49}-token respectively in places l_{10}, l_{37} and l_{49} with characteristics “Separator of the air”, “Separator of the sulfuric acid 98%” and “Separator of the oven gas”,
- β_{13}, β_{27}, β_{40}, β_{43}, β_{46}-token respectively in places l_{13}, l_{27}, l_{40}, l_{43} and l_{46} with characteristics “Heat Exchanger 1”, “Heat Exchanger 2”, “Heat Exchanger 3”, “Heat Exchanger 4” and “Heat Exchanger 5”,
- β_{17} and β_{20}-token respectively in places l_{17} and l_{20} with characteristic “Washing tower-1” and “Washing tower-2”,
- β_{23}-token in place l_{23} with characteristic “Drying tower”,
- β_{30}-token in place l_{30} with characteristic “Oleum absorber”,
- β_{34}-token in place l_{34} with characteristic “Monohydrate absorber”,
- β_{51} and β_{58}-token respectively in places l_{51} and l_{58} with characteristic “Converter (Catalytic layer 1)” and “Converter (Catalytic layers 2, 3, 4, 5)”,

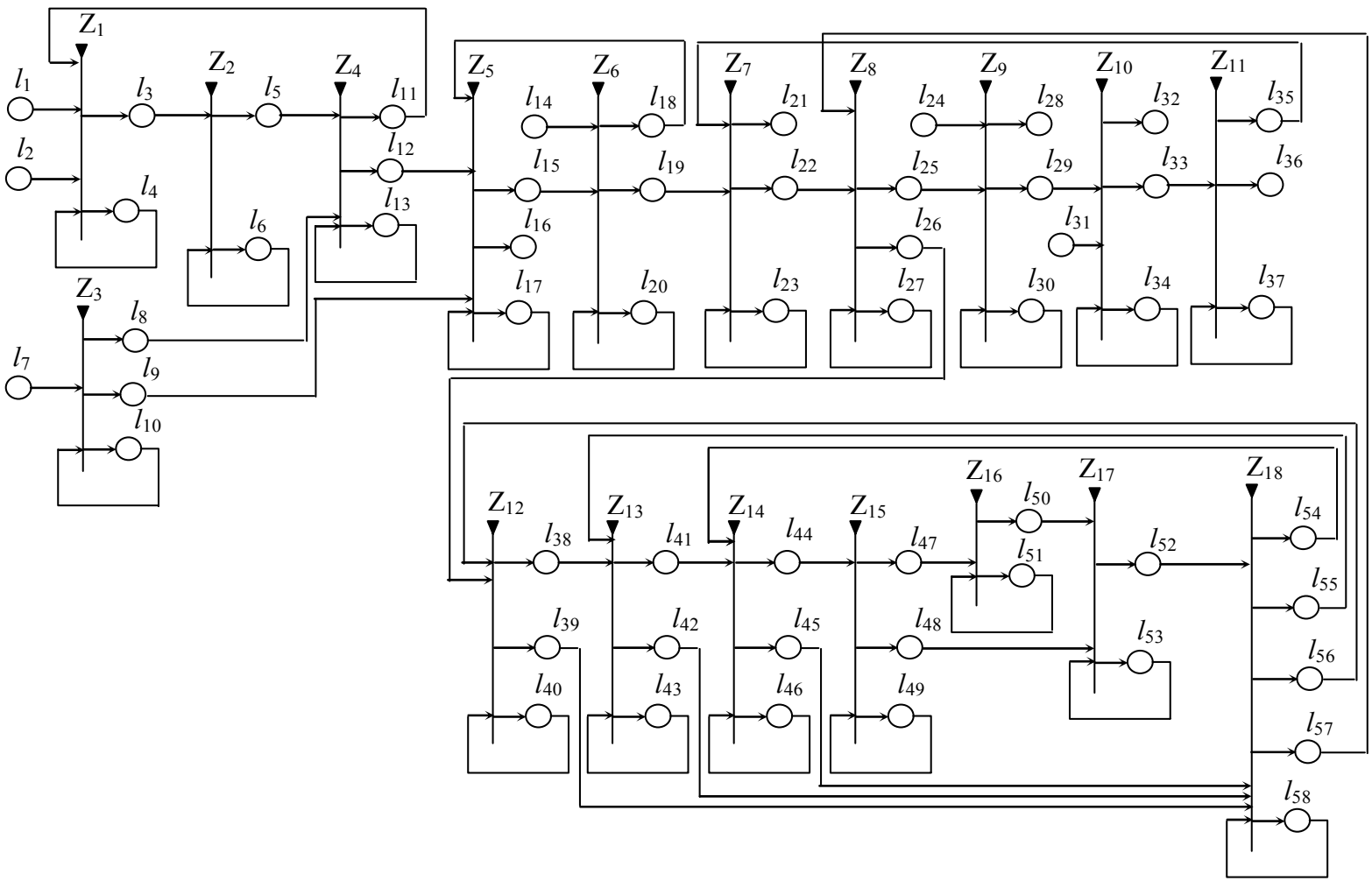

Fig. 2. The GN model of the process of production of sulfuric acid from waste sulfuric acid

- β_{53}-token in place l_{53} with characteristic “Mixer”.

This β-tokens will be in their own places during the whole time during which the GN functions.

From places l_1 and l_2 come respectively α_1 and α_2-tokens with characteristic “Waste sulfuric acid with temperature 25°C and amount 376,80 kg/t product” and “H_2S-gas with temperature 47°C and amount 93,78 kg/t product”.

$$Z_1 = <\{ l_1, l_2, l_4, l_{11}\}, \{ l_3, l_4\}, R_1, \vee(\wedge(l_1, l_2, l_{11}), l_4) >,$$

where

$$R_1 = \begin{array}{c|cc} & l_3 & l_4 \\ \hline l_1 & false & true \\ l_2 & false & true \\ l_4 & W_{4,3} & true \\ l_{11} & false & true \end{array},$$

and

$W_{4,3}$ = “There is oven gas”.

The token entering place l_3 obtains the charateristic

“Oven gas with temperature 920°C and amount 1174,15 kg/t”.

$$Z_2 = <\{l_3, l_6 \}, \{l_5, l_6\}, R_2, \vee(l_3, l_6)>,$$

where

$$R_2 = \begin{array}{c|cc} & l_5 & l_6 \\ \hline l_3 & false & true \\ l_6 & W_{6,5} & true \end{array},$$

and

$W_{6,5}$ = “There is cooled oven gas”.

The token entering place l_5 obtains the charateristic

“Oven gas with temperature 420°C and amount 1174,15 kg/t”.

From place l_7 comes α_7-token with characteristic “Air from atmospheric, temperature 25°C, amount 1377,48 kg/t product”.

$$Z_3 = <\{l_7, l_{10} \}, \{l_8, l_9, l_{10}\}, R_3, \vee(l_7, l_{10}) >,$$

where

$$R_3 = \begin{array}{c|ccc} & l_8 & l_9 & l_{10} \\ \hline l_7 & false & false & true \\ l_{10} & true & true & true \end{array}.$$

On the first activation of the transition Z_3 the α_{10}-token enters in place l_{10} and do not obtains new characteristic. On the next activation of the transition Z_3 the α_{10}-token splits into two new tokens (α_{10}', α_{10}'') that enter places l_8 and l_9 whit charateristic

“Air, temperature 25°C, amount 704,19 kg/t” and

“Air, temperature 25°C, amount 673,29 kg/t”.

$$Z_4 = <\{l_5, l_8, l_{13}\}, \{l_{11}, l_{12}, l_{13}\}, R_4, \vee(\wedge(l_5, l_8), l_{13}) >,$$

where

$$R_4 = \begin{array}{c|ccc} & l_{11} & l_{12} & l_{13} \\ \hline l_5 & false & false & true \\ l_8 & false & false & true \\ l_{13} & W_{13,11} & W_{13,12} & true \end{array},$$

and:

$W_{13,11}$ = "There is air",

$W_{13,12}$ = "There is oven gas".

The α-tokens from places l_5 and l_8 merges in place l_{13}. It generates two new tokens that enters places l_{11} and l_{12} whit charateristic respectively:

"Air with temperature 300°C, amount 704,19 kg/t" and

"Oven gas with temperature 240°C, amount 1174,15 kg/t".

$$Z_5 = <\{l_9, l_{12}, l_{17}, l_{18}\}, \{l_{15}, l_{16}, l_{17}\}, R_5, \vee(\wedge(l_9, l_{12}, l_{18}), l_{17}) >,$$

where

$$R_5 = \begin{array}{c|ccc} & l_{15} & l_{16} & l_{17} \\ \hline l_9 & false & false & true \\ l_{12} & false & false & true \\ l_{17} & W_{17,15} & W_{17,16} & true \\ l_{18} & false & false & true \end{array},$$

and:

$W_{17,15}$ = "There is a oven gas after washing tower 1",

$W_{17,16}$ = "There is a 12% sulfuric acid".

The α-tokens entering places l_{15} and l_{16} obtain charateristic respectively:

"Oven gas after washing tower 1, temperature 80°C, amount 1911,02 kg/t"

"12 % sulfuric acid, temperature 75°C, amount 131,69 kg/t".

From place l_{14} comes α_{14}-token with characteristic "Water".

$$Z_6 = <\{ l_{14}, l_{15}, l_{20}\}, \{ l_{18}, l_{19}, l_{20} \}, R_6, \vee(\wedge(l_{14}, l_{15}), l_{20})>,$$

where

$$R_6 = \begin{array}{c|ccc} & l_{18} & l_{19} & l_{20} \\ \hline l_{14} & false & false & true \\ l_{15} & false & false & true \\ l_{20} & W_{20,18} & W_{20,19} & true \end{array},$$

and:

$W_{20,18}$ = "There is an acid water",

$W_{20,19}$ = "There is an oven gas to the drying tower".

The tokens entering places l_{18} and l_{19} obtain the charateristic respectively:

"Acid water, 70°C, amount 195,26 kg/t" and

"Gas to the drying tower, 40°C, amount 1733,97 kg/t".

$$Z_7 = <\{l_{19}, l_{23}, l_{35}\}, \{ l_{21}, l_{22}, l_{23}\}, R_7, \vee(\wedge(l_{19}, l_{35}), l_{23}) >,$$

where

$R_7 =$

	l_{21}	l_{22}	l_{23}
l_{19}	*false*	*false*	*true*
l_{23}	$W_{23,21}$	$W_{23,22}$	*true*
l_{35}	*false*	*false*	*true*

and:

$W_{23,21}$ = "There is a 93 % sulfuric acid",

$W_{23,22}$ = "There is an oven gas from the drying tower".

The α-tokens entering places l_{21} and l_{22} obtain charateristics

"93 % sulfuric acid 50°C, amount 1409,46 kg/t" and

"Gas from the drying tower, 70°C".

$$Z_8 = <\{ l_{22}, l_{27}, l_{57}\}, \{l_{25}, l_{26}, l_{27}\}, R_8, \vee(\wedge(l_{22}, l_{57}), l_{27}) >,$$

where

$R_8 =$

	l_{25}	l_{26}	l_{27}
l_{22}	*false*	*false*	*true*
l_{27}	$W_{27,25}$	$W_{27,26}$	*true*
l_{57}	*false*	*false*	*true*

and:

$W_{27,25}$ = "There is a gas to the oleum absorber",

$W_{27,26}$ = "There is a gas to the Heat Exchanger 3".

The α-tokens entering places l_{25} and l_{26} obtain charateristics

"Gas to the oleum absorber, 200°C, amount 1658,53 kg/t" and

"Gas to the Heat Exchanger 3".

From place l_{24} comes α_{24}-token with characteristic "20 % oleum".

$$Z_9 = <\{l_{24}, l_{25}, l_{30}\}, \{l_{28}, l_{29}, l_{30}\}, R_9, \vee(\wedge(l_{24}, l_{25}), l_{30}) >,$$

where

$R_9 =$

	l_{28}	l_{29}	l_{30}
l_{24}	*false*	*false*	*true*
l_{25}	*false*	*false*	*true*
l_{30}	$W_{30,28}$	$W_{30,29}$	*true*

and:

$W_{30,28}$ = "There is oleum",

$W_{30,29}$ = "There is a gas to the Monohydrate absorber".

The α-tokens entering places l_{28} and l_{29} obtain charateristics

"Oleum, product, 70°C, amount 966,64 kg/t" and

"Gas to the Monohydrate absorber, 60°C, amount 1336,98 kg/t".

From place l_{31} comes α_{31}-token with characteristic "98 % sulfuric acid".

$$Z_{10} = <\{l_{29}, l_{31}, l_{34}\}, \{l_{32}, l_{33}, l_{34}\}, R_{10}, \vee(\wedge(l_{29}, l_{31}), l_{34})>,$$

where

$$R_{10} = \begin{array}{c|ccc} & l_{32} & l_{33} & l_{34} \\ \hline l_{29} & false & false & true \\ l_{31} & false & false & true \\ l_{34} & W_{34,32} & W_{34,33} & true \end{array},$$

and:
$W_{34,32}$ = "There is a gas to the atmosphere",
$W_{34,33}$ = "There is a 98 % H_2SO_4".

The α-tokens entering places l_{32} and l_{33} obtain charateristics

"Gas to the atmosphere, 50°C, amount 1199,04 kg/t" and "98 % H_2SO_4".

$$Z_{11} = <\{l_{33}, l_{37}\}, \{l_{35}, l_{36}, l_{37}\}, R_{11}, \vee(l_{33}, l_{37})>,$$

where

$$R_{11} = \begin{array}{c|ccc} & l_{35} & l_{36} & l_{37} \\ \hline l_{33} & false & false & true \\ l_{37} & W_{37,35} & W_{37,36} & true \end{array},$$

and:
$W_{37,35}$ = "There is a 98 % sulfuric acid",
$W_{37,36}$ = "There is a 98 % H_2SO_4 product".

The α-tokens entering places l_{35} and l_{36} obtain charateristics

"98 % sulfuric acid, 30°C, amount 1334,02 kg/t" and
"98 % H_2SO_4 product, 65°C, amount 1000 kg".

$$Z_{12} = <\{l_{26}, l_{40}, l_{56}\}, \{l_{38}, l_{39}, l_{40}\}, R_{12}, \vee(\wedge(l_{26}, l_{56}), l_{40})>,$$

where

$$R_{12} = \begin{array}{c|ccc} & l_{38} & l_{39} & l_{40} \\ \hline l_{26} & false & false & true \\ l_{40} & W_{40,38} & W_{40,39} & true \\ l_{56} & false & false & true \end{array},$$

and:
$W_{40,38}$ = "There is an oven gas",
$W_{40,39}$ = "There is a SO_3 gas to the layer 3".

The α-tokens entering places l_{38} and l_{39} obtain charateristics

"Oven gas, amount 1658,53 kg/t" and
"SO_3 gas to the layer 3, 450°C, amount 1658,33 kg/t".

$$Z_{13} = <\{l_{38}, l_{43}, l_{55}\}, \{l_{41}, l_{42}, l_{43}\}, R_{13}, \vee(\wedge(l_{38}, l_{55}), l_{43})>,$$

where

$$R_{13} = \begin{array}{c|ccc} & l_{41} & l_{42} & l_{43} \\ \hline l_{38} & false & false & true \\ l_{43} & W_{43,41} & W_{43,42} & true \\ l_{55} & false & false & true \end{array},$$

and:
$W_{43,41}$ = "There is an oven gas"
$W_{43,42}$ = "There is a SO_3 gas to the layer 4".

The α-tokens entering places l_{41} and l_{42} obtain charateristics

"Oven gas, amount 1658,53 kg/t" and
"SO_3 gas to the layer 4, 435°C, amount 1658,33 kg/t".

$$Z_{14} = <\{l_{41}, l_{46}, l_{54}\}, \{l_{44}, l_{45}, l_{46}\}, R_{14}, \vee(\wedge(l_{41}, l_{54}), l_{46})>,$$

where

$$R_{14} = \begin{array}{c|ccc} & l_{44} & l_{45} & l_{46} \\ \hline l_{41} & false & false & true \\ l_{46} & W_{46,44} & W_{46,45} & true \\ l_{54} & false & false & true \end{array},$$

and:
$W_{46,44}$ = "There is an oven gas",
$W_{46,45}$ = "There is a SO_3 gas to the layer 5".

The α-tokens entering places l_{44} and l_{45} obtain charateristics
"Oven gas, amount 1658,53 kg/t" and
"SO_3 gas to the layer 5, 430°C, amount 1658,53 kg/t".

$$Z_{15} = <\{l_{44}, l_{49}\}, \{l_{47}, l_{48}, l_{49}\}, R_{15}, \vee(l_{44}, l_{49})>,$$

where

$$R_{15} = \begin{array}{c|ccc} & l_{47} & l_{48} & l_{49} \\ \hline l_{44} & false & false & true \\ l_{49} & W_{49,47} & W_{49,48} & true \end{array},$$

and:
$W_{49,47}$ = "There is an oven gas to the Converter (Catalytic layer 1)",
$W_{49,48}$ = "There is an oven gas to the Mixer".

The α-tokens entering places l_{47} and l_{48} obtain charateristics
"Oven gas to the Converter (Catalytic layer 1), 440°C, amount 1330,37 kg/t" and
"Oven gas to the mixer, 440°C, amount 328,16 kg/t".

$$Z_{16} = <\{ l_{47}, l_{51}\}, \{l_{50}, l_{51}\}, R_{16}, \vee(l_{47}, l_{51})>,$$

where

$$R_{16} = \begin{array}{c|cc} & l_{50} & l_{51} \\ \hline l_{47} & false & true \\ l_{51} & W_{51,50} & true \end{array},$$

and
$W_{51,50}$ = "There is a SO_3 gas after the layer 1".

The α-token entering place l_{50} obtains charateristic
"SO_3 gas after the layer 1, 580°C, amount 1330,37 kg/t".

$$Z_{17} = <\{l_{48}, l_{50}, l_{53}\}, \{l_{52}, l_{53}\}, R_{17}, \vee(\wedge(l_{48}, l_{50}), l_{53})>,$$

where

$$R_{17} = \begin{array}{c|cc} & l_{52} & l_{53} \\ \hline l_{48} & false & true \\ l_{50} & false & true \\ l_{53} & W_{53,52} & true \end{array},$$

and

$W_{53,52}$ = "There is cooled gas".

The token entering place l_{52} obtains the charateristic

"SO_3 gas to the Converter (Catalytic layers 2, 3, 4, 5), 470°C, amount 1658,33 kg/t".

$$Z_{18} = <\{l_{39}, l_{42}, l_{45}, l_{52}, l_{58}\}, \{l_{54}, l_{55}, l_{56}, l_{57}, l_{58}\}, R_{18}, \vee(l_{39}, l_{42}, l_{45}, l_{52}, l_{58}) >,$$

where

$$R_5 = \begin{array}{c|ccccc} & l_{54} & l_{55} & l_{56} & l_{57} & l_{58} \\ \hline l_{39} & false & false & false & false & true \\ l_{42} & false & false & false & false & true \\ l_{45} & false & false & false & false & true \\ l_{52} & false & false & false & false & true \\ l_{58} & W_{58,54} & W_{58,55} & W_{58,56} & W_{58,57} & true \end{array},$$

and:

$W_{58,54}$ = "There is a SO_3 gas to the Heat Exchanger 5 (from layer 4)",

$W_{58,55}$ = "There is a SO_3 gas from the layer 3",

$W_{58,56}$ = "There is a SO_3 gas from the layer 2",

$W_{58,57}$ = "There is a SO_3 gas to the Heat Exchanger 2".

The α-tokens entering places l_{54}, l_{55}, l_{56} and l_{57} obtain charateristic respectively:

"SO_3 gas to the Heat Exchanger 5, 430°C, amount 1658,53 kg/t",

"SO_3 gas from the layer 3, 540°C, amount 1658,53 kg/t",

"SO_3 gas to the Heat Exchanger 2, 460°C, amount 1658,53 kg/t" and

"SO_3 gas after from the layer 4, 436°C, 1658,53 kg/t".

4. Conclusion

The process of production of sulfuric acid from waste sulfuric acid was described by generalized nets. The use of hierarchical operators, which could model the same transition at each place in more detail, would make the model more concrete. Most of the model parameters can also be regarded as characteristics of tokens from an additional contour, thus achieving optimization with respect to our given aim. Statistical information would need to be collected in order to monitor the development of the process.

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