Manual and Computer-Aided Calculation of the Energy Balance of Processes with Recycle Streams

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Abstract: A manual and a computer-aided method for the calculation of the energy balance of processes with recycle streams have been presented. The method emphasizes that the material balances of the processes need to have been calculated by one of the well-known methods of calculating the material balances of such processes. The results demonstrate that for large and complex processes involving several recycle streams, computer-aided calculation is imperative.

Key words: Energy balance calculation, streams with recycle, computer-aided calculation thermodynamic, Nigeria

INTRODUCTION

The first law of thermodynamics which is also known as the law of conservation of energy, states that energy cannot be destroyed or created. Energy can only be transformed from one form to the other. Thus, the total energy entering any system must be exactly equal to that leaving the system plus any accumulation of energy within the system. A mathematical expression of this principle is termed an energy balance.

A material balance and an energy balance are together of primary importance in chemical engineering process design. In any energy balance, as in a material balance, the inputs are equated against the outputs plus any accumulation of energy within the system, over a unit period of time in flow process or for a given cycle or batch of operation in the case of a non-flow process.

Theory: The General Energy Equation for a system can be set up by considering the various types of energy which can possibly exist in the system, if electrostatic and magnetic forms of energy are neglected (Aneke and Oyoh, 2008; Aneke, 2009):

$$\sum m_1 U_1 + \sum m_1 P_1 V_1 + \sum \frac{m_1 \bar{u}_1^2}{2g_c} +$$

$$\sum m_1 Z_1 \frac{g}{g_c} + \sum m_1 Es_1 + Q =$$

$$\sum m_2 U_2 + \sum m_2 P_2 V_2 + \sum \frac{m_2 \bar{u}_2^2}{2g_c} +$$

$$\sum m_2 Z_2 \frac{g}{g_c} + \sum m_2 Es_2 + W + \Delta E \tag{1}$$

Where:
m_1 = The initial mass of the system
m_2 = The final mass of the system
U_1 = The initial internal energy of the system
$\bar{u}_1$ = The initial bulk velocity of the system
Z_1 = The initial height of the system above a datum level
Z_2 = The final height of the system above the same datum level
g = The local value of the acceleration due to gravity
g_c = Dimensional constant
E_s = The surface energy per unit mass of the system
Q = The net energy added to the system as heat
W = The net energy removed from the system as work done by the system on the surrounding
ΔE = The net change of energy within the system
P_1 = The initial pressure of the system
P_2 = The final pressure of the system
V_1 = The initial volume of the system
V_2 = The final volume of the system
$\bar{u}_2$ = The final bulk velocity of the system
U_2 = The final internal energy of the system

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In specific cases, the General Energy Equation, Eq. 1, assumes simpler forms (Aneke, 2009). Specifically, many flow processes of the type encountered in chemical engineering practice are characterized by large internal energy changes. They also possess relatively small energy values associated with work and changes in potential, kinetic and surface energies. In such cases, the General Energy Equation, Eq. 1 reduces to:

$$\Sigma m_2 (U_2 + P_2 V_2) - \Sigma m_1 (U_1 + P_1 V_1) = Q \qquad (2)$$

Equation 2 may be satisfactorily applied to the great majority of transformation processes where the primary objective is manufacture as in a chemical plant and not the production of power as in a power generating plant. However, whenever Eq. 2 is applied, it must be borne in mind that it is only an approximation which was arrived at by neglecting certain terms in the General Energy Equation, Eq. 1, such as shaft work and changes in potential, kinetic and surface energies. The significance or otherwise of the neglected terms should be verified when there is doubt.

The General Energy Equation for flow processes, Eq. 2 shows that the term (U + PV) occurs repeatedly in these equations. As a result of the frequent occurrence of this term, Kamerlingh Onnes (1853-1926) in 1909 proposed that the term be designated by the name enthalpy and by the symbol H. Thus:

$$H = U + PV \qquad (3)$$

For industrial chemical processes, the kinetic energy, potential energy, surface energy and shaft work terms in the General Energy Equation. Equation 1 are negligible or cancel out and the heat added is equal to the increase in enthalpy:

$$Q = \Delta H \qquad (4)$$

The distinction between increase of enthalpy and addition of heat must be kept constantly in mind. The relationship between the heat transferred to a substance and its temperature is given by the Eq. 5:

$$dQ = nCdT \qquad (5)$$

Where:
n = The number of moles
C = The molar heat capacity

The heat capacity per mole of substance and dT is the temperature rise caused by the quantity of heat dQ. If a unit mass is taken as the basis for heat capacity, Eq. 5 becomes:

$$dQ = mCdT \qquad (6)$$

Where m represents mass and C is heat capacity per unit mass or specific heat. It must be emphasized that heat is not a state property. Like work (W) the amount of heat required to produce a given change in state depends on the particular process or path taken. Thus, heat is a path function. It follows also that the heat capacity of a substances depends on the path followed. Heat capacities are usually defined for only two paths, constant volume Cv and constant pressure Cp.

These quantities are state properties because there is no ambiguity about the path to which they apply. For a homogeneous material, they depend on temperature and pressure just as specific volume and density do.

For a reversible constant volume non-flow process involving 1 mol of an ideal gas, from the first law of thermodynamics:

$$dU = dQ = CvdT \qquad (7)$$
and
$$\Delta U = Q = \int CvdT \qquad (8)$$

Equation 7 and 8 show that for such a process, the change in internal energy is equal to the heat added. For a reversible constant pressure non-flow process, involving 1 mol of an ideal gas, from the first law of thermodynamics:

$$dH = dQ = CpdT \qquad (9)$$
and
$$\Delta H = Q = \int CpdT \qquad (10)$$

The quantities that depend in the path, viz. dQ and Q, are given by Eq. 9 and 10 for reversible processes only because Eq. 9 and 10 were derived from the first law of thermodynamics for a reversible process. However, H, Cp and dT are state properties of the system and changes in these properties do not depend on path.

Although, the relationships dH = CpdT and ΔH = $\int$ CpdT were derived for a reversible process at constant pressure, they must apply to all processes that cause the same change in state.

Therefore, it is correct to state that dH = CpdT and ΔH = $\int$ CpdT for any process for which $P_1 = P_2$, whether reversible or whether actually carried out at constant pressure or not. However, it is only for the reversible constant pressure path that heat and work can be obtained from the equations.

$$dQ = dH,$$
$$dQ = CpdT,$$
$$Q = \Delta H,$$
$$Q = \int CdpT$$
$$dW = PdV$$
$$W = P\Delta V$$

As is the case with internal energy, absolute values of the enthalpy of any substance are unknown. However, accurate values can be determined relative to some arbitrarily chosen standard state. The temperature, form of aggregation and pressure of the substance at the standard state must be clearly specific. The values of the enthalpy so determined with reference to the standard state are relative enthalpies that is relative to the chosen standard state. For example, the standard state for the enthalpy of any component or stream of components in a process may be taken as the gas at 298 K and 1 atm. The standard state temperature may be chosen for the sake of convenience.

Heat balance is a loose term which has come into general use in all thermal processes in which changes in kinetic energy, potential energy and shaft work are negligible. Therefore, heat balance is a special type of energy balance. For processes where the types of energy just mentioned can be neglected, so-called heat-balances may be applied to flow processes at any pressure and to non-flow processes at constant pressure. The General Energy Equation, Eq. 1 earlier, shows that neither heat balance nor enthalpy balance in the general case is an appropriate term. Thus, the use of the term heat balance or enthalpy balance should be discouraged because it is misleading. Therefore, it is advisable that all such balances be referred to by the correct term of energy balance, even when kinetic energy, potential energy and shaft work are negligible.

In applying the General Energy Equation, Eq. 1, both mass and energy remain constant, ΔEs (surface energies) and the kinetic energy terms are usually negligible, the potential energy terms usually cancel and the equation reduces to:

$$Q = \Sigma m_2 H_2 - \Sigma m_1 H_1 + W \qquad (11)$$

The shaft work term, W, in Eq. 11 is the net value of the work added to the system and the work supplied by the turbine. In chemical processes, W may be neglected because it is usually negligible when compared with the total energy balance of the process. In processes where the work (W) is negligible, such as those encountered in the chemical industry, the heat transferred is equal to the change in enthalpy and Eq. 11 reduces to:

$$Q = \Sigma m_2 H_2 - \Sigma m_1 H_1 = \Delta H \qquad (12)$$

In the same way, in non-flow processes at constant pressure where work other than that of expansion is negligible, the heat transferred is equal to the change in enthalpy. However, where work and kinetic and potential energies are not negligible or in non-flow processes at constant volume, the change in enthalpy is not equal to the heat transferred. Thus, the distinction between change in enthalpy and amount of heat transferred must be clearly borne in mind. For any process for which $P_2 = P_1$, (constant P) whether carried out at constant pressure or not:

$$\Delta H = \int_{T_0}^{T} CpdT \qquad (13)$$

If, in addition, the process is reversible as well as constant pressure, then:

$$Q = \Delta H = \int_{T_0}^{T} CpdT \qquad (14)$$

Where:
T_0 = The standard state temperature
T = The actual temperature of the substance

If heat capacity, Cp is assumed independent of temperature, Eq. 14 can be readily evaluated. However, such an assumption is rarely valid and in general the equation can be integrated only when the heat capacity is known as a function of temperature. The heat capacities of gases are also functions of pressure.

However, the heat capacities of real gases are not required to evaluate such thermodynamic properties of real gases as enthalpy and internal energy. This is because ideal gas heat capacities are sufficient and available. The heat capacities of gases in the ideal gas state are different for different gases. However, heat capacities for the ideal gas state are independent of pressure and are functions of temperature only. The temperature dependence is often given by two empirical equations:

$$C'p = \alpha + \beta T + \gamma T^{-2} \qquad (15)$$

$$C'p = a + bT + cT^{-2} \qquad (16)$$

Where Cp is the ideal gas heat capacity, α, β, γ, a, b and c are constants characteristic of the gas considered, T is absolute temperature.

MATERIALS AND METHODS

The procedure for calculating the enthalpies of gases and liquids relative to a standard state: As in the study the absolute value of the enthalpy of a substance is unknown. However, the enthalpy of a given substance

relative to a standard or reference state may be calculated from its thermodynamic properties. The standard state can be chosen arbitrarily for convenience. Let us assume that the standard state chosen is the gas at 298 K and 1 atm. The enthalpy of a substance is calculated as the change in enthalpy in passing from the state of aggregation of the substance at the standard state where the enthalpy is assumed to be equal to zero to the state of aggregation of the substance at the existing condition. As was discussed earlier at constant pressure the increase in enthalpy is equal to the heat absorbed. Normally, at moderate pressures, the effect of pressure on the enthalpy of liquids and solids may be assumed to be negligible, except when the existing conditions are close to the critical point. The effect of pressure on the enthalpy of gases can usually not be assumed to be negligible and must usually be taken into consideration. For a gaseous component or gaseous mixture of components, the enthalpy of the component, H, at TK is determined by simply calculating the sensible heat involved in taking the component or components from 298 K to TK that is:

$$H = F \int_{298}^{T} C'p(g) dT \qquad (17)$$

Where:

F = The molar flow rate of the component
$C'p(g)$ = The ideal gas molar heat capacity of the component
T = The absolute temperature (TK)

Since T>298 K, the enthalpy of a gaseous component or a gaseous mixture of components, H is positive. For a liquid component or a liquid mixture of components, the enthalpy H, at TK is made up of two components:

The sensible heat component, H1, involved in taking the liquid component or components from 298 K to TK, that is:

$$H1 = F \int_{298}^{T} Cp(1) dT \qquad (18)$$

Where:

F = The molar flow rate of the component
Cp(1) = The liquid molar heat capacity of the component
T = The absolute temperature (TK)

The latent heat component, H2, involved in taking the liquid component or components to the gaseous state at 298 K that is:

$$H2 = F\lambda_{298} \qquad (19)$$

Where F is the molar flow rate of the component λ_{298} is the molar latent heat of vaporization of the component at 298 K. The total enthalpy of the liquid component:

$$H = H1 + H2 = F \left(\int_{298}^{T} Cp(1) dT - \lambda_{298} \right) \qquad (20)$$

Since T>298 K, H1 is positive. Since heat is absorbed in the vaporization process at 298 K, H2 is negative. If the latent heat component, H2 is larger than the sensible heat component, H1 of the enthalpy of a liquid component, then the total enthalpy, H of the liquid component or a liquid mixture of components is negative that is:

$$H = F \left(\int_{298}^{T} Cp(1) dT - \lambda_{298} \right) \qquad (21)$$

If the latent heat component, H2 is smaller than the sensible heat component, H1 of the enthalpy of a liquid component, the total enthalpy, H of the liquid component or a liquid mixture of component is positive that is:

$$H = F \left(\int_{298}^{T} Cp(1) dT - \lambda_{298} \right) \qquad (22)$$

Thus, heat evolved in bringing a component to the standard state is a positive contribution to its enthalpy, while heat absorbed in bringing a component to the standard state is a negative contribution to its enthalpy. The procedure described before is shown in Fig. 1. If the pressure of a stream is not 1 atm, the effect on its enthalpy of changing its pressure to the standard state pressure of 1 atm must be taken into consideration unless it can be assumed that the effect of pressure on the enthalpy of the stream can be neglected.

Process description: The process used to describe the proposed method is the synthesis of cumene (isopropylbenzene) from benzene and propylene shown as a process flow diagram in Fig. 2.
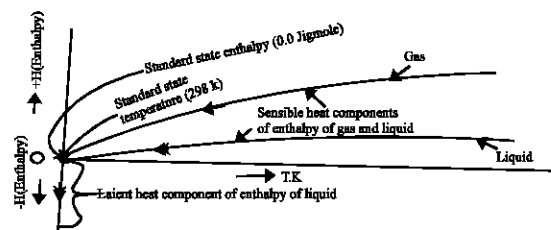

Fig. 1: Aschematic idealization of the calculation of the enthalpies of gases and liquids relative to the standard state (the gas at 298 K and 1 atm)
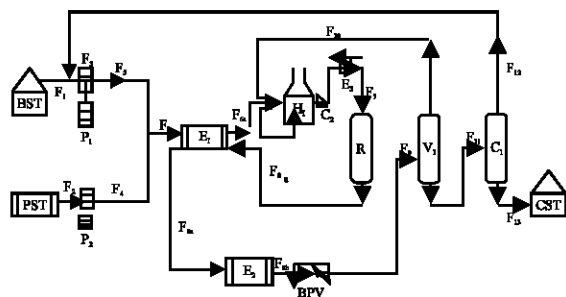
Fig. 2: The manufacture of cumene

Process equipment: BST = Benzene storage tank; PST = Propylene storage tank; P_1 = Benzene pump; P_2 = Propylene pump; E_1 = Reactor effluent heat exchanger; H_1 = Furnace; R = Fixed bed catalytic reactor; E_2 = Flash vessel heat exchanger; V_1 = Flash vessel; C_1 = Distillation Column; BPV = Back pressure valve; C_2 = Compressor; E_3 = Heat exchanger; CST = Cumene storage tank.

Process stream: F_1 = Pure benzene feed; F_2 = Pure propylene feed; F_3 = Benzene make up (F1) + Benzene recycle (F_{12}); F_4 = Propylene pump exit stream; F_5 = Benzene pump exit stream; F_6 = Benzene stream (F_5) + propylene stream (F4); F_{6a} = Heat exchanger (EI) outlet stream; F_7 = Reactor inlet stream; F_8 = Reactor outlet stream; F_{8a} = Heat exchanger outlet stream; F_{8b} = Back pressure valve inlet stream; F_9 = Flash vessel inlet stream; F_{10} = Flash vessel outlet stream; F_{11} = Flash vessel outlet vapour stream; F_{12} = Distillation column liquid stream; F_{13} = Distillation column bottom stream.

The reaction is given by the following stoichiometric equation:

$$C_6H_{6(g)} + C_3H_{6(g)} \rightleftharpoons C_9H_{12(g)}$$
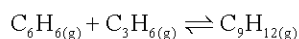
In this process, cumene is produced by passing a gaseous mixture of benzene and propylene over a suitable catalyst in a tubular reactor (R). The reactants are pumped from storage tanks are mixed and are allowed to exchange heat with the reactor effluent stream in a heat exchanger. E_1 are vaporized in a furnace H_1 are compressed to the reaction pressure of 30 atm in a compressor C_2 are adjusted to the reaction temperature of 623 K (350°C) in a heat exchanger E_3 and are fed to the reactor. The product gases exchange heat with the reactor inlet stream in the heat exchanger E_1. The product gases are further cooled in another heat exchange E_2 to condense essentially all the cumene and unreacted benzene in the product stream. The unreacted propylene in the product stream is completely separated from the liquid component of the reactor effluent stream in a low pressure separator V_1 which is maintained at 1 atm pressure and 623 K (350°C). The propylene is used to fire the furnace.
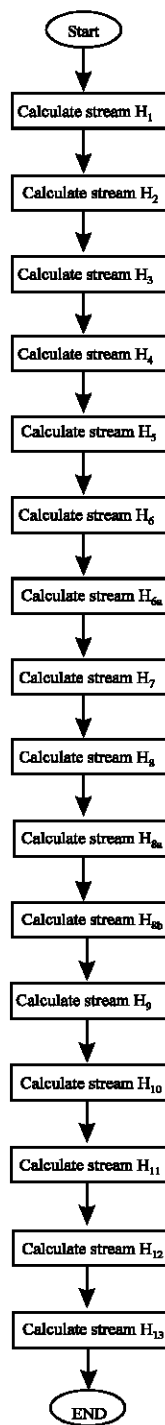

Fig. 3: The block diagram of the calculations

The liquid stream from the separator is fed to a distillation column, C_1 which separates the benzene from the cumene. The cumene product stream leaves at the bottom of the column while the benzene stream leaves at the top and is recycled to the fresh benzene feed stream.

Table 1: The stream flow rates from the material balance calculation (Cycle 4 is the authentic material balance of the process) (Aneke and Oyoh, 2008; Aneke , 2009)

Stream	Component	Cycle			
		1	2	3	4
1	Benzene (gmol s^{-1})	64.94	26.11	29.39	29.39
	Propylene (gmol s^{-1})	-	-	-	-
	Cumene (gmol s^{-1})	-	-	-	-
2	Benzene (gmol s^{-1})	-	29.23	-	-
	Propylene (gmol s^{-1})	32.47	-	29.23	29.23
	Cumene (gmol s^{-1})	-	-	-	-
3	Benzene (gmol s^{-1})	64.94	58.45	58.45	58.45
	Propylene (gmol s^{-1})	-	-	-	-
	Cumene (gmol s^{-1})	-	3.21	3.21	3.21
4	Benzene (gmol s^{-1})	-	-	-	-
	Propylene (gmol s^{-1})	32.47	29.23	29.23	29.23
	Cumene (gmol s^{-1})	-	-	-	-
5	Benzene (gmol s^{-1})	64.94	58.45	58.45	58.45
	Propylene (gmol s^{-1})	-	-	-	-
	Cumene (gmol s^{-1})	-	3.21	3.21	3.21
6	Benzene (gmol s^{-1})	64.94	58.45	58.45	58.45
	Propylene (gmol s^{-1})	32.47	29.23	29.23	29.23
	Cumene (gmol s^{-1})	-	3.21	3.21	3.21
6a	Benzene (gmol s^{-1})	64.94	58.45	58.45	58.45
	Propylene (gmol s^{-1})	32.47	29.23	29.23	29.23
	Cumene (gmol s^{-1})	-	3.21	3.21	3.21
7	Benzene (gmol s^{-1})	64.94	58.45	58.45	58.45
	Propylene (gmol s^{-1})	32.47	29.23	29.23	29.23
	Cumene (gmol s^{-1})	-	3.21	3.21	3.21
8	Benzene (gmol s^{-1})	32.79	29.51	29.51	29.51
	Propylene (gmol s^{-1})	0.32	0.29	0.29	0.29
	Cumene (gmol s^{-1})	32.15	32.15	32.15	32.15
8a	Benzene (gmol s^{-1})	32.79	29.51	29.51	29.51
	Propylene (gmol s^{-1})	0.32	0.29	0.29	0.29
	Cumene (gmol s^{-1})	32.15	32.15	32.15	32.15
8b	Benzene (gmol s^{-1})	32.79	29.51	29.51	29.51
	Propylene (gmol s^{-1})	0.32	0.29	0.29	0.29
	Cumene (gmol s^{-1})	32.15	32.15	32.15	32.15
9	Benzene (gmol s^{-1})	32.79	29.51	29.51	29.51
	Propylene (gmol s^{-1})	0.32	0.29	0.29	0.29
	Cumene (gmol s^{-1})	32.15	32.15	32.15	32.15
10	Benzene (gmol s^{-1})	-	-	-	-
	Propylene (gmol s^{-1})	0.32	0.29	0.29	0.29
	Cumene (gmol s^{-1})	-	-	-	-

Design data: The following design data apply:

- Quantity of cumene in the cumene product stream is 100,000 metric tons per stream year
- Basis of calculation is 8000 h per stream year
- Reactor temperature is 623 K (350°C)
- Reactor pressure is 30 atm
- The molar ratio of benzene to propylene in the reactor inlet stream is 2:1
- The conversion of propylene in the reactor is 99%
- The product cumene purity level is 99% (wt.) the balance being benzene
- The recycle benzene purity is 90% (wt.) the balance being cumene
- The cumene going into the distillation column that leaves in the cumene product stream is 90% (wt.)
- Assume that all vapours are ideal gases and that all liquid mixtures are ideal solutions

The block diagram for the calculations, using the procedure described earlier is shown in Fig. 3. No iterative procedure is required in the calculation of the enthalpies of the streams.

The calculations of the stream enthalpies (H) make use of the results of the stream molar flow rates from the material balance calculation of the same process which have been reported else where (Aneke and Oyoh, 2008; Aneke, 2009). These stream flow rates from the material balance calculation are shown in Table 1.

In the enthalpy calculations, a correlation expressing the constant pressure heat capacities of the components as a function of temperature in a power series was used for liquids and was obtained from Perry *et al.* (1997) while a correlation for gases was obtained from Reid *et al.* (1977). The heat of vaporization λ_{298} of the components was evaluated using a correlation obtained from Perry *et al.* (1997).

RESULTS AND DISCUSSION

The complete energy balance using the procedure outlined before was solved manually. It was also solved using a computer programme written in the visual basic computer language.

The computer solution followed the same procedure outlined in the manual calculation described in Sections 3.0 and 4.0 before and shown as a block diagram in Fig. 3. The manual calculations are available in Aneke (2009), while the computer calculations are available in Ike (2007).

The result of the manual solution is shown in Table 2. The result of the computer solution is virtually identical with that of the manual solution and is, therefore not shown here. The difference between the manual and the computer generated enthalpies of the streams is <0.01 in every case.

The procedure described earlier has been used to calculate the energy balance for the industrial synthesis of cumene from benzene and propylene at 623 K (350°C) and 30 atm. Manual and computer-aided calculations were both used.

The results obtained in both calculations are virtually identical. The manual calculations required several man-hours.

The calculations involved in the simple illustrative example described earlier show that for large and more complex processes involving more recycle streams, the manual calculations would consume many man-days of work. The results of the manual and computer-aided calculations clearly demonstrate that for such processes computer-aided calculation is imperative.

Table 2: The result of the manual enthalpy calculations

Stream	Propylene (kcal s^{-1})	Benzene (kcal s^{-1})	Cumene (kcal s^{-1})	Total (kcal s^{-1})	Temperature (K)	Pressure (atm)
F_1	-	-215.25	-	-215.25	318.00	1.00
F_2	-76.82	-	-	-76.82	318.00	20.00
F_3	-	-392.14	-29.18	-421.32	339.00	1.00
F_4	-76.82	-	-	-76.82	318.00	30.00
F_5	-	-392.14	-29.18	-421.32	339.00	30.00
F_6	-46.75	-380.74	-28.36	-455.85	333.00	30.00
F_{6a}	-3.42	-254.20	-17.27	-274.89	405.00	30.00
F_7	275.11	808.01	46.71	1127.83	623.00	30.00
F_8	2.78	408.79	777.79	1187.31	623.00	30.00
F_{8a}	2.03	345.07	659.25	10006.35	547.00	30.00
F_{8b}	0.53	79.73	151.81	232.07	368.00	30.00
F_9	0.53	-170.73	-244.05	-414.25	368.00	1.00
F_{10}	0.53	-	-	0.53	368.00	1.00
F_{11}	-	-170.73	-244.08	-414.78	368.00	1.00
F_{12}	-	-177.21	-26.09	-203.30	356.00	1.00
F_{13}	-	-1.81	-138.30	-140.11	421.00	1.00

CONCLUSION

A method for the calculation of the energy balance of processes with recycle streams has been presented. The method begins with a calculation of the material balance of the process, using any of the well-known methods, viz. The Cut and Try method (Sinnott, 1999; Henley and Rosen, 1969) and the formal algebraic method or their variations (Sinnott, 1999; Reklaitis and Schneider, 1983; Aneke and Oyoh, 2008). The method outlined before has been used to calculate the energy balance of the industrial synthesis of cumene from benzene and propylene at 623 K (350°C) and 30 atm. The results of the manual and computer-aided calculations clearly demonstrate that for large and complex processes, involving several recycle streams, computer aided calculation is imperative.

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