# Infinite Dimensional Port Hamiltonian Representation of reaction diffusion processes $^{\star}$

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**Abstract:** In this paper is proposed a thermodynamically consistent port Hamiltonian formulation of non isothermal reaction diffusion processes. The use of appropriate thermodynamic variables for the definition of the state and the co-state vectors allows to highlight the inherent infinite dimensional interconnection structure linking the different thermodynamic phenomena (entropy production, diffusion, conduction) that is suitable for control purposes. The presentation is given for systems defined on one dimensional spatial domain.

*Keywords:* Port Hamiltonian Systems, Distributed Systems, Irreversible Thermodynamics

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## 1. INTRODUCTION

The Port Hamiltonian framework is based on a geometric description of physical systems and is particularly useful for the modeling and control of multi-physics, network and distributed parameters systems (Duindam et al., 2002). Since its definition (Maschke *et al.*, 1992) and its extension to distributed parameter systems (Maschke *et al.*, 2000; Le Gorrec *et al.*, 2005) it has been widely and successfully applied to classical mechanical and electrical systems, both in finite and infinite dimensions (Duindam et al., 2002; Hamroun *et al.*, 2010; van der Schaft *et al.*, 2014). The application of Port Hamiltonian formalism to thermodynamic systems (Baaiu et al., 2009) is much more tedious as in the general non isothermal case the link between energy and irreversible phenomena cannot be associated to a linear geometric structure (Eberard *et al*, 2004). Nevertheless slightly degenerated structures suitable for control purposes can be defined as it has been the case for continuous finite dimensional stirred tank reactors (CSTR) (Hoang *et al.*, 2011).

The idea of this paper is to propose a proper decomposition of thermodynamic phenomena in the case of non isothermal distributed reaction diffusion systems in order to highlight the inherent interconnection structure, called *Stokes Dirac structure* (Maschke *et al.*, 2005). The irreversibility is taken into account through an appropriate non linear closure relation between extended port variables, as it can be done for purely dissipative systems. We discuss how the states and port variables have to be chosen such that geometric properties of the model are emphasized.

It is important to notice that the port based representation proposed in this paper differs from the one in (Zhou *et al.*, 2012) since the skew symmetric operator that defines the geometric structure does not depend on the effort variables. In the present paper all the non linear terms are gathered in the closure relation, accounting for the irreversible phenomena. Such formulation can be advantageously used for control purposes.

The paper is organized as follows. In Section 2, we recall the main properties of irreversible thermodynamic distributed parameter systems. In Section 3 we briefly recall the general port Hamiltonian formulation of distributed parameter systems. In Section 4, we present the model of the reaction diffusion process. In Section 5 is given the port Hamiltonian formulation of the overall system.

## 2. THERMODYNAMIC OVERVIEW FOR DISTRIBUTED PARAMETER SYSTEMS

In Thermodynamics, as far as distributed parameter systems are concerned, the following form of the Gibbs equation is used (De Groot et al (1983)):

$$\mathrm{d}u = T\mathrm{d}s - P\mathrm{d}v + \sum_{i=1}^{n_c} \mu_i \mathrm{d}\omega_i \tag{1}$$

where $u, s, v, \omega_i$ are respectively the energy per unit mass, entropy per unit mass, volume per unit mass and the mass fraction of species $i$. $T$ is the temperature, $P$ the pressure and $\mu_i$ the chemical potential of species $i$. Then the local equilibrium hypothesis for distributed system is expressed in its local form by (see De Groot et al (1983) for details):

$$\frac{Du}{Dt} = T\frac{Ds}{Dt} - P\frac{Dv}{Dt} + \sum_{i=1}^{n_c} \mu_i \frac{D\omega_i}{Dt} \tag{2}$$

where $\frac{D\bullet}{Dt}$ stands for the material derivative $\frac{\partial \bullet}{\partial t} + v_m \frac{\partial \bullet}{\partial z}$ of quantity $\bullet$ per unit mass.

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For simplicity in the remainder of the section we consider that volumes are cylinders of section $\overline{S}$ and that homogeneity properties are assumed such that only the longitudinal coordinate $z$ is necessary. We also assume an incompressible fluid phase and a constant total mass density $\rho$. This implies that $\frac{Dv}{Dt} = \frac{D(\frac{1}{\rho})}{Dt} = 0$. We consider also that the average velocity $v_m$ is constant. Moreover since no convection transport is assumed we have $v_m = 0$.

Then for any sub domain $z \in [z_a, z_b]$ in the reactor, we obtain the integral form of (2):

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{z_a}^{z_b} \rho u(z,t)\overline{S}\mathrm{d}z = & \int_{z_a}^{z_b} T\frac{\partial \rho s(z,t)}{\partial t}\overline{S}\mathrm{d}z \\ & + \sum_{i=1}^{n_c}\int_{z_a}^{z_b} \mu_i \frac{\partial \rho\omega_i(z,t)}{\partial t}\overline{S}\mathrm{d}z \end{aligned} \tag{3}$$

Equation (3) expresses the conservation of energy of the distributed systems without convection.

From the Gibbs equation (2) the pairings of energy conjugated variables are: ($\rho s$, $T$) and ($\rho\omega_i$, $\mu_i$). The time derivative of Gibbs equation (3) associated with the local equilibrium hypothesis shows the natural power conjugated variables given by ($\frac{\partial \rho s}{\partial t}$, $T$) and ($\frac{\partial \rho\omega_i}{\partial t}$, $\mu_i$).

## 3. DISTRIBUTED PORT-HAMILTONIAN SYSTEMS WITH DISSIPATION

The port Hamiltonian formulation of distributed parameter systems is based on a generalization of the finite dimensional Dirac structure introduced in (Courant , 1990; Dorfman , 1993). This geometrical structure relates the flow and effort variables variables through a skew symmetric operator which interprets the power conservation principle.

Let us consider the 1-D port Hamiltonian system with dissipation defined on the $\mathcal{Z} = [a,b]$ with distributed control input defined by:

$$\frac{\partial x}{\partial t} = (\mathcal{J} - \mathcal{G}D\mathcal{G}^\star)\frac{\delta H}{\delta x} + \mathcal{B}u \tag{4}$$

where $x(t,z) = (q,p) \in \mathbb{R}^{2n}$ is the state, $u(t,z) \in C^\infty(\mathcal{Z})$ is the distributed control, $\mathcal{J} = \begin{bmatrix} 0 & I_n \\ I_n & 0 \end{bmatrix} \frac{\partial}{\partial z}$ is a formally skew symmetric differential operator, $\mathcal{G}$ and $\mathcal{B}$ are linear bounded operators with their respective adjoint operator $\mathcal{G}^*$ and $\mathcal{B}^*$, $D \in \mathbb{R}^{2n\times 2m}$ is a non negative definite matrix and $H(x)$ is the Hamiltonian of the system:

$$H(x) = \frac{1}{2}\int_a^b \mathcal{H}dz = \frac{1}{2}\int_a^b x^T\mathcal{L}x\ dz \tag{5}$$

with $\mathcal{L} > 0$ a constant matrix. $\frac{\delta H}{\delta x} = \mathcal{L}x$ represents the variational derivative of the functional $H$ (see Duindam et al. (2002)). Consider the flow variables vector noted $f = (f_q, f_p) = \frac{\partial x}{\partial t} \in C^\infty(\mathcal{Z})^{2n}$ and the effort variables vector $e = (e_q, e_p) = \frac{\delta H}{\delta x} \in C^\infty(\mathcal{Z})^{2n}$.

The model (4) can be written in extended form as

$$\begin{pmatrix} f \\ e_r \end{pmatrix} = \underbrace{\begin{pmatrix} \mathcal{J} & \mathcal{G} \\ -\mathcal{G}^\star & 0 \end{pmatrix}}_{\mathcal{J}_e} \begin{pmatrix} e \\ f_r \end{pmatrix} + \begin{pmatrix} \mathcal{B} \\ 0 \end{pmatrix} u \text{ with } f_r = De_r \tag{6}$$

with a specific dissipative port variables $(f_r, e_r) \in C^\infty(\mathcal{Z})^{2m} \times C^\infty(\mathcal{Z})^{2m}$. Let us define extended flow and effort variables $f_e = (f, f_r)$ and $e_e = (e, e_r)$.

We associate to this system the set of boundary conditions at $a$ and $b$ (a part of them can be used for control purpose) in the case of $\mathcal{G}$ is a matrix ( 0-order differential operator) of:

$$e_\partial = \begin{pmatrix} e_\partial^a(t) \\ e_\partial^b(t) \end{pmatrix} = \begin{pmatrix} -e_q|_a \\ -e_q|_b \end{pmatrix} \ , \ f_\partial = \begin{pmatrix} f_\partial^a(t) \\ f_\partial^b(t) \end{pmatrix} = \begin{pmatrix} e_p|_a \\ e_p|_b \end{pmatrix} \tag{7}$$

*Remark 1.* In the case of the operator $\mathcal{G}$ is of higher dimension, the set of corresponding boundary variables $(f_{e_\partial}, e_{e_\partial})$ could be chosen using the parametrization given in Le Gorrec *et al.* (2005).

The energy balance is given by

$$\frac{dH}{dt} = \frac{1}{2}\frac{d}{dt}\int_a^b x^T\mathcal{L}x\ dz = \int_a^b e^T\frac{\partial x}{\partial t}dz = < e, f > \tag{8}$$

which finally leads to equation (9):

$$\begin{aligned}\frac{dH}{dt} &= {e_\partial^b}^T f_\partial^b - {e_\partial^a}^T f_\partial^a + \int_a^b e^T\mathcal{B}u - \overbrace{e^T\mathcal{G}}^{-e_r^T}\overbrace{D\mathcal{G}^\star e}^{-f_r}\, dz \\ &= {e_\partial^a}^T f_\partial^a - {e_\partial^b}^T f_\partial^b - < y, u > - < e_r, f_r > \end{aligned} \tag{9}$$

with $y = -\mathcal{B}^* e$.

First let us define the space of flow variables

$$\mathcal{F} = \left\{ \begin{pmatrix} f_e \\ f_\partial \\ u \end{pmatrix} \in C^\infty(\mathcal{Z})^{2(n+m)} \times \mathbb{R}^{n\times\{a,b\}} \times C^\infty(\mathcal{Z}) \right\} \tag{10}$$

and the space of effort variables

$$\mathcal{E} = \left\{ \begin{pmatrix} e_e \\ e_\partial \\ y \end{pmatrix} \in C^\infty(\mathcal{Z})^{2(n+m)} \times \mathbb{R}^{n\times\{a,b\}} \times C^\infty(\mathcal{Z}) \right\} \tag{11}$$

endowed with the following non-degenerated bilinear pairing:

$$\begin{aligned}\left\langle \begin{pmatrix} e_e \\ e_\partial \\ y \end{pmatrix} \middle| \begin{pmatrix} f_e \\ f_\partial \\ u \end{pmatrix} \right\rangle = & < e_e, f_e > + < y, u > \\ & + < e_\partial^b, f_\partial^b >_{\mathbb{R}^n} - < e_\partial^a, f_\partial^a >_{\mathbb{R}^n} \end{aligned} \tag{12}$$

which is the duality product defined on the space of effort and flow variables. This power product expresses at the same time the energy balance equation of the system. the notation $<,>_{\mathbb{R}^n}$ stands for the scalar product in $\mathbb{R}^n$. Let us also consider symmetric pairing:

$$\left\langle\left\langle \begin{bmatrix} e_1 \\ f_1 \end{bmatrix}, \begin{bmatrix} e_2 \\ f_2 \end{bmatrix} \right\rangle\right\rangle = < e_1|f_2 > + < e_2|f_1 > \tag{13}$$

where $\begin{bmatrix} e_1 \\ f_1 \end{bmatrix}, \begin{bmatrix} e_2 \\ f_2 \end{bmatrix} \in \mathcal{E} \times \mathcal{F}$

*Definition 1.* (Maschke *et al.* (2005)) A Stokes Dirac structure $\mathcal{D}$ is a subspace of $\mathcal{E} \times \mathcal{F}$ that is maximally isotropic respectively to the non-degenerate symmetric bilinear form (12) or $\mathcal{D}^{\perp} = \mathcal{D}$, $\mathcal{D}^{\perp} = \Big\{ b \in \mathcal{E} \times \mathcal{F} | \, \langle\langle b, b^T \rangle\rangle = 0 \Big\}$.

It can be shown that the subset $\mathcal{D}$:

$\mathcal{D} = \Big\{ (f_e, f_\partial, u, e_e, e_\partial, y) \in \mathcal{E} \times \mathcal{F}$ with (6), $y = -\mathcal{B}^* e$, and $e_\partial = \begin{pmatrix} e_\partial^a \\ e_\partial^b \end{pmatrix}$, $f_\partial = \begin{pmatrix} f_\partial^a \\ f_\partial^b \end{pmatrix} \Big\}$ is a Stokes-Dirac structure with respect to (12).

More generally a Stokes Dirac structure can be obtained for linear first order port-Hamiltonian systems with

$$\mathcal{J} = P_1 \frac{\partial}{\partial z} + P_0 \tag{14}$$

where the matrix $P_1$ is invertible and self-adjoint, and $P_0$ is skew-adjoint (see Le Gorrec *et al.* (2005); Jacob *et al.* (2012)).

## 4. MODEL OF DIFFUSION REACTION PROCESS

We suppose isobaric operating conditions and a constant total mass density $\rho$ inside the jacketed reactor. The reactor is assumed to have a length $L$.

The chemical reaction $r$ involves two species $A$ and $B$: $\nu_A A \longrightarrow \nu_B B$ with stoichiometric coefficients $\nu_A, \ \nu_B > 0$. The reaction kinetics is modeled by a Arrhenius law

$$r = k_0 e^{-\frac{E}{RT}} c_A \tag{15}$$

where $c_A$ is the molar concentration of the specie A, $E$ is the activation energy, $R$ the perfect gas constant and $k_0$ the kinetic constant.

We assume that matter diffusion and heat conduction are occurring inside the reactor.

The diffusion flux $f_d^A$ of species $A$ is given by (see Bird (2002)):

$$f_d^A = -D \partial_z (\mu_A - \mu_B) \tag{16}$$

where $x$ is the state vector and $D$ the diffusion coefficient. Since it is assumed pure diffusion, we have $f_d^A + f_d^B = 0$.

The conduction flux satisfies the Fourier's law:

$$f_F = -\lambda \partial_z (T) \tag{17}$$

where $\lambda > 0$ is the thermal conductivity of the matter.

Furthermore we consider that there is distributed heat transfer $q(z)$ between the reactor and its jacket. We do not develop this term that is in general linear with respect to reactor temperature $T(z)$.

The model for the reaction diffusion system is given by:

$$\begin{cases} \rho \partial_t \omega_A = -\partial_z f_d^A - M_A \nu_A r \\ \rho \partial_t \omega_B = -\partial_z f_d^B + M_B \nu_B r \\ \rho \partial_t s = -\partial_z f^s - \dfrac{q}{T_j} + \sigma \end{cases} \tag{18}$$

where $\omega_i$ represents the mass fraction of the species $i$ ( $i = A, \ B$) and $s$ is the entropy per mass unit. $M_i$ is the molar mass of species $i$, $T_j$ is the distributed temperature of the jacket, $f^s = \sum_{i=A,B} f_d^i s_i + f_F^s$ is the total entropy flux where $f_F^s = \frac{f_F}{T}$ is the entropy flux due to conduction $f_F^s = \frac{f_F}{T}$ and $s_i$ the partial mass entropy of species $i$.

$\sigma$ is the irreversible production of entropy. This term is computed by equalizing the entropy balance given by eq. (18) and the one deduced from the Gibbs equation (2). For this purpose the energy balance is needed. The energy balance with incompressible and isobaric assumptions is expressed through the enthalpy balance:

$$\rho \partial_t h = -\partial_z f^h - q \tag{19}$$

where $h = u + P \frac{1}{\rho}$ is the enthalpy per mass unit and $f^h$ is the total enthalpy flux given by:

$$f^h = f_d^h + f_F \tag{20}$$

where $f_d^h = \sum_{i=A,B} f_d^i h_i$ is the enthalpy flux due to diffusion. $h_i$ is the partial mass enthalpy of species $i$.

The irreversible production of entropy is given by:

$$\begin{aligned} \sigma = & \overbrace{q(\frac{1}{T_j} - \frac{1}{T})}^{\sigma_{ext}} \overbrace{-\frac{r}{T}\mathcal{A}}^{\sigma_r} \overbrace{-\frac{1}{T} f_d^A \partial_z \mu_A}^{\sigma_A} \\ & \overbrace{-\frac{1}{T} f_d^B \partial_z \mu_B}^{\sigma_B} \overbrace{-f^s \frac{\partial_z T}{T}}^{\sigma_S} \end{aligned} \tag{21}$$

with $\mathcal{A} = -\nu_A M_A \mu_A + \nu_B M_B \mu_B$ the chemical affinity.

Each term of the irreversible entropy production terms is assumed in the context of irreversible Thermodynamics to be positive (see Callen (1985)). The first term $\sigma_{ext}$ is related to the exchanges with the jacket of the reactor. The second term $\sigma_r$ is due to the chemical reaction. $\sigma_A$ and $\sigma_B$ are due to diffusion of species A and B in the material domain. Finally $\sigma_S$ is due to diffusion and conduction in the thermal domain.

## 5. PORT HAMILTONIAN FORMULATION FOR DIFFUSION REACTION PROCESSES

In the framework of irreversible Thermodynamics the natural state vector $x$ of the system is given by $x^T = (\, \rho\omega_A \quad \rho\omega_B \quad \rho s \,)$ corresponding to the variable appearing in the material derivative of the local equilibrium equation (2). The energy is then an implicit variable obtained from eq. (2). We call this representation *Implicit energy representation.*

In the sequel of this section we show this *Implicit energy representation* can be written using a Stokes Dirac structure defined on a particular extended pairings of effort and flow variables given in Table 1.

For that purpose we consider the vectors $E \in \mathbf{E} = (H^2[0, L])^3 \times (H^1[0, L])^3 \times (L^2[0, L])^5$ and $F \in \mathbf{F} = (L^2[0, L])^3 \times (H^1[0, L])^3 \times (L^2[0, L])^5$:

$$\begin{aligned} E &= (\, e_A \ \ e_B \ \ e_s \ \ f_A \ \ f_B \ f_s \ f_r \ f_{\sigma_A} \ f_{\sigma_B} \ f_{\sigma_S} \ f_{\sigma_r} \,)^T \\ F &= (\, F_A \ F_B \ F_s \ E_A \ E_B \ E_s \ E_r \ e_{\sigma_A} \ e_{\sigma_B} \ e_{\sigma_S} \ e_{\sigma_r} \,)^T \end{aligned} \tag{22}$$

The subset :

$$(\, f_A \ \ f_B \ f_s \ f_r \ f_{\sigma_A} \ f_{\sigma_B} \ f_{\sigma_S} \ f_{\sigma_r} \,)^T$$

of vectors $E$ and the subset:

$$(\, E_A \ E_B \ E_s \ E_r \ e_{\sigma_A} \ e_{\sigma_B} \ e_{\sigma_S} \ e_{\sigma_r} \,)^T$$

Table 1. variables settings

| flows | | efforts | |
|---|---|---|---|
| $F_A$ | $= \rho\partial_t\omega_A$ | $e_A$ | $= \mu_A$ |
| $F_B$ | $= \rho\partial_t\omega_B$ | $e_B$ | $= \mu_B$ |
| $F_s$ | $= \rho\partial_t s$ | $e_s$ | $= T$ |
| $f_A$ | $= f_d^A$ | $E_A$ | $= -\partial_z\mu_A$ |
| $f_B$ | $= f_d^B$ | $E_B$ | $= -\partial_z\mu_B$ |
| $f_s$ | $= f_d^s$ | $E_s$ | $= -\partial_z T$ |
| $f_r$ | $= r$ | $E_r$ | $= \mathcal{A}$ |
| $f_{\sigma_A}$ | $= -\sigma_A$ | $e_{\sigma_A}$ | $= T$ |
| $f_{\sigma_B}$ | $= -\sigma_B$ | $e_{\sigma_B}$ | $= T$ |
| $f_{\sigma_S}$ | $= -\sigma_s$ | $e_{\sigma_S}$ | $= T$ |
| $f_{\sigma_r}$ | $= -\sigma_r$ | $e_{\sigma_r}$ | $= T$ |
| $u$ | $= -\frac{q}{T}$ | $y$ | $= T$ |

of vector $F$ correspond to the extended effort $e_r$ and flow variables $f_r$ described in section 3.

The model of reaction diffusion system given in (18) can be rewritten as:

$$\begin{cases} F = J_e E + \mathcal{B}_e u \\ y = -\mathcal{B}_e^\star E \end{cases} \tag{23}$$

with $\mathcal{B}_e = \begin{pmatrix} \mathcal{B} \\ 0_3 \\ 0_5 \end{pmatrix}$ where $\mathcal{B} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$. $J$ is a skew-symmetric differential operator given by:

$$J_e = P_1\partial_z + P_0 \tag{24}$$

with

$$P_1 = \begin{pmatrix} 0_3 & -I_3 & 0 \\ -I_3 & 0_3 & 0 \\ 0 & 0 & 0_5 \end{pmatrix} \qquad P_0 = \begin{pmatrix} 0_3 & 0_3 & P \\ 0_3 & 0_3 & 0 \\ -P^T & 0 & 0_5 \end{pmatrix} \tag{25}$$

where $0_3,\ I_3 \in \mathbb{R}^{3\times 3}$, represent the zero matrix and the identity matrix respectively. The two matrices $I_3$ of $P_1$ are related to the diffusion and conduction phenomena.

and

$$P = \begin{pmatrix} -\nu_A M_A & 0 & 0 & 0 & 0 \\ \nu_B M_B & 0 & 0 & 0 & 0 \\ 0 & -1 & -1 & -1 & -1 \end{pmatrix} \tag{26}$$

Let us consider the following boundary port variables:

$$\begin{pmatrix} f_\partial \\ e_\partial \end{pmatrix} = \begin{pmatrix} I_3 & 0 \\ 0 & -I_3 \end{pmatrix} \begin{pmatrix} f|_{\partial z} \\ e|_{\partial z} \end{pmatrix} \tag{27}$$

with

$$e|_{\partial z} = \begin{pmatrix} e_A \\ e_B \\ e_s \end{pmatrix} |_{0,L}, f|_{\partial z} = \begin{pmatrix} f_A \\ f_B \\ f_s \end{pmatrix} |_{0,L} \tag{28}$$

The proposed representation of the system (18) given in (23) is based on an extension of port variables set (flows and efforts) corresponding to the natural dual variables for diffusion, reaction, conduction phenomena but also for their respective entropy production. The system (23) shows that the externalization of the constitutive equations of the previously cited thermodynamic phenomena as well as the irreversible entropy production terms exhibits the intrinsic interconnection structure for the considered system.

This methodology corresponds to "open" the R and the S bonds of the RS bond graph element (see Duindam et al. (2002) for RS elements). This element is used as soon as the entropy balance is written. This power continuous element is formed by a resistive part R that represents the dissipation of some phenomenon with constitutive law between the effort $e_R$ and the flow variable $f_R$: $e_R = R(f_R)$. Since the internal energy is conservative this dissipation appears as a source term S in the thermal domain. The additional port which is endowed with a pair of conjugate variables $(\sigma, T)$ satisfies the power continuity relation: $T\sigma = e_R f_R$, $\sigma$ is the entropy production associated with the phenomenological law defined by R.

Set $\mathcal{F} = \left\{ \begin{bmatrix} F \\ u \\ f_\partial \end{bmatrix} \in \mathbf{F} \times L^2[0, L] \times \mathbb{R}^{3\times\{0,L\}} \right\}$ and $\mathcal{E} = \left\{ \begin{bmatrix} E \\ y \\ e_\partial \end{bmatrix} \in \mathbf{E} \times L^2[0, L] \times \mathbb{R}^{3\times\{0,L\}} \right\}$. Let us endow the subspaces $\mathcal{E}$ and $\mathcal{F}$ with the pairing

$$\begin{aligned} < \begin{bmatrix} E \\ u \\ e_\partial \end{bmatrix} \mid \begin{bmatrix} F \\ u \\ f_\partial \end{bmatrix} > &:= < E, F >_{L^2} + < y, u >_{L^2} \\ &+ < e_\partial^L, f_\partial^L >_{R^3} - < e_\partial^0, f_\partial^0 >_{R^3} \end{aligned} \tag{29}$$

*Proposition 1.* The linear subset $\mathcal{D} \subset \mathcal{E} \times \mathcal{F}$ defined by: $\mathcal{D} = \left\{ \left( \begin{bmatrix} F \\ u \\ f_\partial \end{bmatrix}, \begin{bmatrix} E \\ y \\ e_\partial \end{bmatrix} \right) \in \mathcal{E} \times \mathcal{F} \middle| \ F = JE + \mathcal{B}_e u\ ,\ y = -\mathcal{B}_e E\ ,\ \begin{bmatrix} f_\partial \\ e_\partial \end{bmatrix}_{(0,L)} \text{ as defined in (27)} \right\}$ is a Stokes Dirac structure with respect to the symmetric pairing (29).

Furthermore the irreversible feature of the system is defined by:

$$-E \begin{pmatrix} 0_3 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & I_4 \end{pmatrix} F > 0 \tag{30}$$

*Proof* To prove that $\mathcal{D}$ is a Dirac structure, we follow the same steps given in (van der Schaft *et al.* (2002)) where we have to show that $\mathcal{D} \subset \mathcal{D}^\perp$ and $\mathcal{D}^\perp \subset \mathcal{D}$.

•$\mathcal{D} \subset \mathcal{D}^\perp$:

We define $< F_i, u_i, f_{\partial_i}, E_i, y_i, e_{\partial_i} >= d_i$ for $i = 1,\ 2$.

Let $d_1 \in \mathcal{D}$, and consider any $d_2 \in \mathcal{D}$ .

We consider the following bilinear form:

$$\begin{aligned} << d_1, d_2 >> &= \int_Z (E_1F_2 + E_2F_1 + y_1u_2 + y_2u_1)dz \\ &+ [e_{\partial_1} f_{\partial_2}]_0^L + [e_{\partial_2} f_{\partial_1}]_0^L \\ &= \int_Z \mathcal{I} dz + \int_{\partial Z} \mathcal{F} dz \end{aligned} \tag{31}$$

where $\mathcal{I}$ is the distributed part and $\mathcal{F}$ is the boundary part.

Using the definition (22) of $E$ and $F$, we have:

$$\begin{aligned}\mathcal{I} = {} & e_{A_1}F_{A_2} + e_{B_1}F_{B_2} + e_{s_1}F_{s_2} + f_{A_1}E_{A_2} + f_{B_1}E_{B_2} \\ & + f_{s_1}E_{s_2} + f_{r_1}E_{r_2} + f_{\sigma_{A_1}}e_{\sigma_{A_2}} + f_{\sigma_{B_1}}e_{\sigma_{B_2}} + f_{\sigma_{S_1}}e_{\sigma_{S_2}} \\ & + f_{\sigma_{r_1}}e_{\sigma_{r_2}} + e_{A_2}F_{A_1} + e_{B_2}F_{B_1} + e_{s_2}F_{s_1} + f_{A_2}E_{A_1} \\ & + f_{B_2}E_{B_1} + f_{s_2}E_{s_1} + f_{r_2}E_{r_1} + f_{\sigma_{A_2}}e_{\sigma_{A_1}} + f_{\sigma_{B_2}}e_{\sigma_{B_1}} \\ & + f_{\sigma_{S_2}}e_{\sigma_{S_1}} + f_{\sigma_{r_2}}e_{\sigma_{r_1}} \end{aligned} \tag{32}$$

By substituting all the flux expressions into (32), we have

$$\begin{aligned} & \mathcal{I} = -\partial_z(e_{A_1}f_{A_2} + e_{B_1}f_{B_2} + e_{s_1}f_{s_2} + e_{A_2}f_{A_1} \\ & + e_{B_2}f_{B_1} + e_{s_2}f_{s_1}) + \underbrace{(e_{s_1}\sigma_2 - e_{s_2}\sigma_1 + e_{s_2}\sigma_1 - e_{s_1}\sigma_2)}_{=0} \\ & + M_A\nu_A(f_{r_2}(-e_{A_1} + e_{B_1} + e_{A_1} - e_{B_1}) \\ & + f_{r_1}(e_{A_2} - e_{B_2} - e_{A_2} + e_{B_2})) \\ & = -\partial_z(e_{A_1}f_{A_2} + e_{B_1}f_{B_2} + e_{s_1}f_{s_2} + e_{A_2}f_{A_1} \\ & + e_{B_2}f_{B_1} + e_{s_2}f_{s_1}) \end{aligned} \tag{33}$$

The sum of the third and fourth line is zero.Thus by integration:

$$\begin{aligned} \int_Z \mathcal{I}dz = {} & -\int_{\partial_z}(e_{A_1}f_{A_2} + e_{B_1}f_{B_2} + e_{s_1}f_{s_2} + e_{A_2}f_{A_1} + \\ & e_{B_2}f_{B_1} + e_{s_2}f_{s_1})dz \\ = {} & -[e_{A_1}f_{A_2}]_0^L - [e_{B_1}f_{B_2}]_0^L - [e_{s_1}f_{s_2}]_0^L \\ & -[e_{A_2}f_{A_1}]_0^L - [e_{B_2}f_{B_1}]_0^L - [e_{s_2}f_{s_1}]_0^L \\ = {} & -e_{\partial_1}f_{\partial_2}|_0 + e_{\partial_1}f_{\partial_2}|_L - e_{\partial_2}f_{\partial_1}|_0 + e_{\partial_2}f_{\partial_1}|_L \end{aligned} \tag{34}$$

Finally

$$\begin{aligned} \int_Z \mathcal{I}dz + \int_{\partial Z}\mathcal{F}dz = {} & -e_{\partial_1}f_{\partial_2}|_0 + e_{\partial_1}f_{\partial_2}|_L - e_{\partial_2}f_{\partial_1}|_0 \\ & + e_{\partial_2}f_{\partial_1}|_L - e_{\partial_1}f_{\partial_2}|_L + e_{\partial_1}f_{\partial_2}|_0 \\ & - e_{\partial_2}f_{\partial_1}|_L + e_{\partial_2}f_{\partial_1}|_0 \\ = {} & 0 \end{aligned} \tag{35}$$

As the result, we have $<< d_1, d_2 >>= 0$, and thus $\mathcal{D} \subset \mathcal{D}^\perp$.

•$\mathcal{D}^\perp \subset \mathcal{D}$:
let us consider $d_1 \in \mathcal{D}^\perp$ , implying that for all elements $d_2 \in \mathcal{D} << d_1, d_2 >>= 0$

First, we assume that the boundary part $e_\partial f_\partial$ is zero, and the reactor is autonomous so that $\int_Z yudz = 0$, implying that

$$\int_Z (E_1F_2 + E_2F_1)dz = 0 \tag{36}$$

We demonstrate that in this case, $F_1$ has the same expression as $F_2$

We replace $F_2$ by the expression as given in Table 1 into the equation (36) because $d_2 \in \mathcal{D}$, we have:

$$\begin{aligned} E_1F_2 = {} & f_{A_2}\partial_z e_{A_1} + f_{B_2}\partial_z e_{B_1} + f_{s_2}\partial_z e_{s_1} + e_{A_2}\partial_z f_{A_1} \\ & + e_{B_2}\partial_z f_{B_1} + e_{s_2}\partial_z f_{s_1} - \partial_z(e_{A_1}f_{A_2} + e_{B_1}f_{A_2} \\ & + e_{s_1}f_{s_2} + e_{A_2}f_{A_1} + e_{B_2}f_{A_1} + e_{s_2}f_{s_1}) \\ & M_A\nu_A(-f_{r_2}e_{A_1} - f_{r_1}e_{A_2} + e_{B_1}f_{r_2} + e_{B_2}f_{r_1}) \\ & + e_{s_1}\sigma_{s_2} - e_{s_2}\sigma_{s_1} \end{aligned}$$

The equation (36) gives that:

$$\begin{aligned} \int_Z E_2F_1dz = {} & -\int_Z E_1F_2dz \\ = {} & -\int_Z (f_{A_2}\partial_z e_{A_1} + f_{B_1}\partial_z e_{B_1} + f_{s_1}\partial_z e_{s_1})dz \\ & -\int_Z (e_{A_2}\partial_z f_{A_1} + e_{B_2}\partial_z f_{B_1} + e_{s_2}\partial_z f_{s_1})dz \\ & \int_Z (M_A\nu_A(f_{r_2}e_{A_1} + f_{r_1}e_{A_2} - e_{B_1}f_{r_2} \\ & -e_{B_2}f_{r_1}) - e_{s_1}\sigma_{s_2} + e_{s_2}\sigma_{s_1})dz \\ & +[e_{A_1}f_{A_2}]_0^L + [e_{B_1}f_{A_2}]_0^L + [e_{s_1}f_{s_2}]_0^L \\ & +[e_{A_2}f_{A_1}]_0^L + [e_{B_2}f_{A_1}]_0^L + [e_{s_2}f_{s_1}]_0^L \end{aligned}$$

By the hypothesis that on the boundary efforts are zero, we eliminate the boundary part so that:

$$\begin{aligned} \int_Z E_2F_1dz = {} & -\int_Z E_1F_2dz \\ = {} & -\int_Z (f_{A_2}\partial_z e_{A_1} + f_{B_1}\partial_z e_{B_1} + f_{s_1}\partial_z e_{s_1})dz \\ & -\int_Z (e_{A_2}\partial_z f_{A_1} + e_{B_2}\partial_z f_{B_1} + e_{s_2}\partial_z f_{s_1})dz \\ & \int_Z (M_A\nu_A(f_{r_2}e_{A_1} + f_{r_1}e_{A_2} - e_{B_1}f_{r_2} \\ & -e_{B_2}f_{r_1}) - e_{s_1}\sigma_{s_2} + e_{s_2}\sigma_{s_1})dz \end{aligned} \tag{37}$$

In the same way we obtain:

$$\begin{aligned} E_2F_1 = {} & e_{A_2}(-\partial_z f_{A_1} + M_A\nu_A f_{r_1}) + e_{B_2}(-\partial_z f_{B_2} \\ & -M_B\nu_B f_{r_1}) + e_{s_2}(-\partial_z f_{d_2}^s + \sigma_{s_1}) \\ & + f_{A_2}(-\partial_z e_{A_1}) + f_{B_2}(-\partial_z e_{B_1}) \\ & + f_{s_2}(-\partial_z e_{s_1}) + f_{r_2}(-\nu_A M_A e_{A_1} + \nu_B M_B e_{B_1}) \\ & -(\sigma_{A_2} + \sigma_{B_2} + \sigma_{S_2} + \sigma_{r_2})e_{s_1} \end{aligned} \tag{38}$$

By identification , we easily find that for $F_1$:

$$\begin{aligned} & F_{A_1} = \rho\partial_t\omega_{A_1} \quad F_{B_1} = \rho\partial_t\omega_{B_1} \quad F_{s_1} = \rho\partial_t\omega_{s_1} \\ & E_{A_1} = -\partial_z\mu_{A_1} \quad E_{B_1} = -\partial_z\mu_{B_1} \quad E_{s_1} = -\partial_z T_1 \\ & E_{r_1} = \mathcal{A}_1 \quad e_{\sigma_{A_1}} = T_1 \quad e_{\sigma_{B_1}} = T_1 \\ & e_{\sigma_{S_1}} = T_1 \quad e_{\sigma_{r_1}} = T_1 \end{aligned} \tag{39}$$

which has the same expression as in the table (1).

Secondly, we consider that the boundary is no longer zero, and demonstrate this part of $d_1$ also belongs to $\mathcal{D}$

let us substitute eq. (39) into (31):

$$\int_0^L (-\partial_z(e_{A_1}f_{A_2} + e_{B_1}f_{B_2} + e_{s_1}f_{s_2} + e_{A_2}f_{A_1} + e_{B_2}f_{B_1} + e_{s_2}f_{s_1}))dz + [e_{\partial_1}f_{\partial_2}]_0^L + [e_{\partial_2}f_{\partial_1}]_0^L = 0 \tag{40}$$

We obtain easily:

$$\begin{aligned} &[e_{\partial_1}f_{\partial_2}]_0^L + [e_{\partial_2}f_{\partial_1}]_0^L \\ &-[e_{A_1}f_{A_2}]_0^L - [e_{B_1}f_{B_2}]_0^L - [e_{s_1}f_{s_2}]_0^L \\ &-[e_{A_2}f_{A_1}]_0^L - [e_{B_2}f_{B_1}]_0^L - [e_{s_2}f_{s_1}]_0^L = 0 \end{aligned} \tag{41}$$

Substituting boundary conditions (28) into (41), we obtain:

$$\begin{aligned} [e_{\partial_2}f_{\partial_1}]_0^L = &[e_{A_2}f_{A_1}]_0^L + [e_{B_2}f_{B_1}]_0^L + [e_{s_2}f_{s_1}]_0^L \\ &[e_{A_1}f_{A_2}]_0^L + [e_{B_1}f_{B_2}]_0^L + [e_{s_1}f_{s_2}]_0^L \\ &-e_{\partial_1}f_{\partial_2}|_L + e_{\partial_1}f_{\partial_2}|_0 \end{aligned}$$

The sum of the second and the third line is zero so that:

$$[e_{\partial_2}f_{\partial_1}]_0^L = -[e_{A_2}f_{A_1}]_0^L - [e_{B_2}f_{B_1}]_0^L - [e_{s_2}f_{s_1}]_0^L$$

As the result , by identification we can easily obtain that $f|_{\partial z_1} = \begin{pmatrix} f_{A_1} \\ f_{B_1} \\ f_{s_1} \end{pmatrix}$ showing that indeed $d_1 \in D$.

- The third point of the proof concerns the irreversibility feature of the representation

It can be easily checked by using Table 1 and expression (21) that

$$\begin{aligned} -E \begin{pmatrix} 0_3 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & I_4 \end{pmatrix} F &= E \begin{pmatrix} 0_3 & 0 & 0 \\ 0 & I_4 & 0 \\ 0 & 0 & 0_4 \end{pmatrix} F \\ &= -r\mathcal{A} - f_d^A \partial_z \mu_A - f_d^B \partial_z \mu_B \\ &\quad - f^s \partial_z T > 0 \end{aligned} \tag{42}$$

□

## 6. CONCLUSION

This paper is a first attempt to the port Hamiltonian representation of a tubular reactor. It is shown how transport phenomena and chemical reactions can be represented in the energy based representation using a Stokes-Dirac structure. It remains to show how the convection phenomenon can be integrated in such formulation. This formulation could be advantageously used for control purposes using the passivity based methods and thermodynamic availability function introduced in Ruszkowski *et al.* (2005) and used for the control of CSTRs in Hoang *et al.* (2011).

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