Improvement of Devulcanization Yield during Reclamation of Waste Tires

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Strictly as per the compliance and regulations of :

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I. Introduction

Estimates of DOT, department of transportation indicate there are 254.4 million registered passenger vehicles in this country, United States as of 2007. The number of passenger vehicles has grown steadily from the year 1960. The per capita car ownership is higher in the United States. In terms of volume, the number of passenger vehicles registered in the first eight months of 2011 in China was 9.83 million [1]. The number tires used in the cars on the road in the Unites States is more than a billion. Over 2 billion waste tires are estimated to be stockpiled in the landfills of this country, United States.

Texas Commission on Environmental Quality has collected data in 2011 about waste tire recycling problem. Nearly one tire for every resident, i.e. 292 million automobile tires is discarded each year. In Texas State 32 million tires were thrown away last year. Per Houston Chronicle [2] 14 million tires in shredded form are allowed to form heaps across Texas. Many more end up south of the border. 5 million tires form a mountain in Odessa and another 809,000 are piled alongside Genoa Red Bluff Road in southeast Houston. Relegation of tires to landfills has been outlawed for the past two decades. This has not stopped the 1 in 10 tires in Texas ending up in the landfill. The Houston Chronicle has received public complaints. 1200 people were upset about illegal piles of tires. These tires collect water and leads to pandemic due to West Nile virus. Tire fires ruins the happy parties creating polluted runoffs. TCEQ has issued 420 citations for illegal tire disposal in the past 5 years. Tire shredders are paid a fee per tire. TCEQ and EPA see cement kilns, paper plants and fuel furnaces using the waste tires. Environmental challenges are faced by 12 million people in the border between Mexico and U.S. A tire mountain in Ciudad Juarez, Mexico across the Rio Grande from El Paso, TX has gone down some from 7 million tires to 2.5 million tires. Engineering students at Institute for Sustainable Energy and Environment at Texas a& M, Kingsville are experimenting with using old tires to build new roads. This study in response to the call in [2] for affordable solutions to the waste tire problem.

Two large tire stockpile fires in St-Am able, Quebec and Hagersville, Ontario in 1989 [3] increased public awareness of the waste tire recycling problem. Large sums of money were invested in the USA in the development of reducing, reusing and recycling-techniques and processes for scrap tires-shredded tires (TDF) in the case of pulp and paper mills, generating stations, and some cement kilns or whole tires for most kilns accounts for 70 to 80% of all recycled tires in North America. Seven years later, it seems this is still the most economical and environmentally acceptable solution. One serious environmental problem related to the transportation field is the stockpiling of old rubber tires [4]. Several huge fires of old tires have already occurred in Canada and the United States and have caused considerable air and possibly soil pollution.

Development of techniques to recycle this potentially valuable material is of increased significance. The focus of current research at the Centre for Surface Transportation. Technology has been to develop a high-performance rubber asphalt concrete based on the stone mastic asphalt (SMA) concept which will be flexible enough (yet strong enough) to resist differential frost heave along roadways better than standard hot-mixed asphalt.. A solution to reduce the littering of the environment is to use ground tire rubber in road construction. Currently, about 27 million tons of asphalt is used each year in road construction and maintenance of the country's 2 million miles of roads. If all of the waste tire rubber could be combined with asphalt in

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road construction, it would displace less than 6% of the total asphalt used each year, yet could save about 60 trillion Btus annually [5].

As the automobile tire technology has grown and met the need for safer and more durable tires, stronger reinforcement and more chemically resistant rubber compounds have made recycling tires more difficult. In an effort to resolve this problem, techniques and equipment were developed to grind tires into small pieces, and new markets were sought to utilize the crumb rubber product streams from ground tires. Industrial combustion processes were modified to accept scrap tires as fuel. These efforts have been beneficial, steadily increasing the percentage of scrap tires recycled to about 10% in 1985, and reaching 72% in 1995. Vulcanized rubber scrap was used as a filler in PE-based and PVC-based compositions intended for manufacturing traffic control equipment elements, viz. road guides, rigid large-sized road emergency sign supports, speed humps, guiding rails etc. The compositions examined were based entirely on recyclates. Rubber scrap was prepared from worn-out tires in particulate form, Segregated and sieved to collect fractions of a suitable particle size. The PE and PVC scraps were obtained from the cable production plant; some containing copper wire bits; reclaimed PEfilm, termed the agglomerate, was also used. Paraffin oil was used as a compatibiliser; EVA was used as an impact strength modifier, and chalk and phosphogypsum (a calcium sulfate waste product from the phosphoric acid process- very difficult to utilize) were used as fillers. Optimum composition formulations were established and verified for making road sign and traffic control equipment elements by injection, & compression molding and extrusion molding techniques [6]. Tire-added latex concrete (TALC) was developed to incorporate recycledtire rubber as part of concrete [7].

Crumb rubbers from tires were used in TALC as a substitute for fine aggregates or styrene-butadiene rubber (SBR) latex, while maintaining the same water cement ratio. Various static and dynamic strengths of TALC were measured and compared to those of conventional and latex-modified concrete. TALC showed higher flexural and impact strengths than those of portland cement and latex-modified and rubber-added concretes. Microscopic pictures taken using the scanning electron microscope (SEM) seem to support thatthere is better bonding between crumb rubbers and portland cement paste due to latex. TALC showed potential of becoming a viable construction material to enhance brittle concrete while incorporating waste tires. Vulcanized rubber scrap was used as a filler in PE-based and PVC-based compositions [8] intended for manufacturing traffic control equipment elements, viz. road guides, rigid large-sized road emergency sign supports, speed humps, guiding rails etc. The compositions examined were based entirely on recycles. Rubber

scrap was prepared from worn-out tires in particulate form, segregated and sieved to collect fractions of a suitable particle size. The PE and PVC scraps were obtained from the cable production plant, some containing copper wire bits; reclaimed PE film, termed the agglomerate, was also used. Paraffin oil was used as a compatibiliser; EVA was used as an impact strength modifier, and chalk and phosphogypsum (a calcium sulfate waste product from the phosphoric acid process, very difficult to utilize) were used as fillers. Optimum composition formulations were established and verified for making road sign and traffic control equipment elements by injection, compression molding and extrusion molding techniques. The technical uses of scrap tires, and the recycling of rubber in the U.S was shown [9] that over 172 million tires, 64% of the total, were used as tire derivative fuel in 1997, representing the single largest use of scrap tires. Other utilizations of scrap time are illustrated. A special feature of this process was that flushing air from the cavity of the machine and blanketing it with nitrogen generally gives a stiffer and less tacky soluble mass. Most vulcanizing processes produce significant amounts of waste and rejects.

A process which can economically reduce this waste to zero was described [10]. Current practiceincludes retreading, recycling as crumb rubber and combustion for thermal energy. A literature review was made to compare the discarded tire recycling practices in the United States, Japan and Korea. The durability of rubber modified mixtures [11] used in paving projects was evaluated. While the presence of moisture affects the adhesion between the binder and the aggregate producing stripping effects, the characteristics of the rubber modified binder is expected to improve the mixture durability and performance. Experience with road fills in Washington State constructed with thick layers of tire chips spontaneously burning has led to a decrease in tire chip use nationally [12]. The rheological properties of composites of recycled high density polyethylene (HDPE) with recycled tire rubber particles at shear rates from 1.167 to 116.7 s^{-1} was studied [13]. The recycling rate of used tires in Japan is much higher [14] than that in other countries. The new Solid-State Shear Extrusion (SSSE) pulverization process can [15]) convert tire rubber and/or plastics into controlled particle size powder in a once through, continuous process using a modified co-rotating twin-screw extruder. Mechanical properties were studied on composites of recycled high density polyethylene (HDPE) and recycled tire rubber particles [16]. Either portland cement or magnesium oxychloride cement was used [17] as binders for concretes that incorporated fine rubber aggregate, ranging from 0 to 25 percent by volume. An experimental study has been conducted to evaluate the effects of incorporating granulated rubber into Portland cement concrete [18]. One potential use of scrap tires

within the civil engineering field, specifically, as a lightweight backfill material for retaining walls, has been investigated [19]. The percentage of rubber products going to landfill have increased dramatically [20]. The value of using crumbed old tires in pavements were recognized in the 1960s. If properly incorporated into pavement, Crumbed rubber can improve asphalt-concrete performance [21]. How tire recyclers are Struggling with ways to make profits from scrap tires was discussed in [22]. A multi-disciplinary Research effort to develop new asphalt materials with improved engineering properties using Different types of modifiers, plus new manufacturing technologies, is underway at the University of Calgary [23]. For Envirotire (Lillington, North Carolina), producing quality Crumb rubber this summer is all in a night's work [24]. The marketplace for recycled products Places substantial demands on suppliers for consistent high quality and production flexibility [25]. Previous attempts to commercialize processes for the pyrolysis of scrap tires are Reviewed [26], and results are presented of research undertaken by the Pyro Division of Svedala Industries in the processing of raw pyrolysis char into pyrolysis carbon black for use as a modifier in asphalt road surfaces. It is reported in this short item that the North American Recycled Rubber Association (NARRA) and two Canadian companies have successfully completed a research project to use recycled tire fibers in the production of rebound carpet cushion [27]). Brief details are provided. Scanning electron microscopy (SEM) was utilized to observe the microstructure and fracture surfaces of tensile, bending, and internal bonding specimens of diphenylmethane diisocyanate (MDI) bonded wood fiber/recycled tire rubber composites [28]

Annual production of polybutadiene is about 2.1 million tons in 2000 [29]. 70% of the PBd goes into tire manufacture. 25% of PBd goes into ABS and HIPS engineering thermoplastics. Vulcanization is used convert synthetic rubber into more durable materials by addition of sulfur. Cross-links are intentionally formed between polymer chains by sulfur bridges. Goodyear invented vulcanization in 1839. In his *Gum-Elastica* he records [30] how the effect of heat on the same compound that had decomposed in mail bags can be charred like leather. The rubber is cured. About 30% of automotive tires are carbon black. Other additives are also added for better balance of properties.

II. Solution to the Tired Old Problem– Reclamation More Valuable Compared to Incineration

Per a patent on depolymerization [31] the total energy required to make 1-3 butadiene monomer is 60,000 BTU per pound. The fuel energy value of tire is approximately 15,000 BTU per pound. The value of the monomer in the waste tires is lot higher than the value attained from using waste tires as fuel. Further the pollution and proliferation of West Nile virus is an added concern. Therefore it would be more profitable and more environmentally benign to reclaim the butadiene and/or the polybutadiene in the waste tires.

2013 would be the centennial of the award of the nobel prize in physics to K. Kamerlingh Onnes for his investigations on the properties of matter at low temperatures. Among other things like liquid Helium, he came up with the Virial equation of state. A careful study of polybutadiene-butadiene reversible polymerization equilibrium at low pressures has not been undertaken. What pressures and temperatures does PBd exist as vapor, gas or supercritical state? What pressures does PBd depolymerize to butadiene monomer? When one were to lower the pressure in the laboratory of a kettle containing PBd which would happen first: (i) vaporization of PBd or ; (ii) depolymerization ?

P-T, Pressure-Temperaturediagrams and zero pressure isotherms can be constructed using the information given in [32] for PBd, polybutadiene. The Tait equation of state (Eq. 2.27) is;

$$V = V_0\left(1 - C\ln\left(1 + \frac{P}{B}\right)\right) \qquad (1)$$

can be used. The Tait parameter B for PBd is given in Table 2.1 in [5] as $1777e^{-3.593E-3T}$. C is taken as 0.0894 and zer pressure isotherm V_0 is given in Table 2.1 in the book as $1.0970e^{6.6E-4T}$.

A side-by side comparison of the predictions of Pressure-Temperature equilibrium for different molecular weights of PBd can be made using: (i) Tait equation; (ii) FOV, Flory Orwoll and Vrij Theory, Eq. (2.37); (iii) Prigogine Square-Well cell model, Eq. (2.40); (iv) lattice fluid theory of Sanchez and Lacombe, Eq. (2.59).

The ceiling temperature of polyalphamethyl styrene is 61 ^{0}C. This is the temperature at which the depolymerization reactions are as favorable as the polymerization reactions. Thermal terpolymeization kinetics for alpha methyl styrene acrylonitrile and styrene was reported at three different temperatures [33]. Approach to reclamation of rubber from waste tires was proposed in [34-39].

The Clapeyron equation for polymerization-depolymerization equilibria was derived [32]. The ceiling temperature of PBd is about 585 ^{0}C at atmospheric pressure. An approximate estimate of the ceiling temperature of PBd at low pressures can be made using the Clapeyron equation as follows;

$$\Delta P = \frac{\Delta H}{\Delta V}\ln\left(\frac{T_2}{T_1}\right) \qquad (2)$$

The enthalpy of polymerization of PBd can be expected to be similar to that of polyethylene and is about -17.4 kcal.mole^{-1}.K^{-1}. The change in density of PBd upon polymerization goes from 640 kg.m^{-3} for 1.3 butadiene monomer to 900-950 kg.m^{-3} for PBd. More refined estimates can be made by allowing for change of volume during polymerization and change of enthalpy during polymerization to vary with change in pressure. Thus Eq. (12.8) can be reintegrated. Another method of simulating the ceiling temperature at low pressures is by use of Eq. (12.43) in [32];

$$T_c = \frac{\Delta H_p}{R \ln(M_e) + \Delta S_p} \qquad (3)$$

The entropy change of polymerization is about 25-30 cal.K^{-1}.mole^{-1} for most polymerization systems by free radical propagation/depropagation.

There can be two approaches to reclamation of rubber from waste tires. One method is by chemical reactions involving devulcanizing and depolymerization and the other is by solvent extraction. The outlines of the two methods are as follows;

Method I A 3 phase Gas-Liquid-Solid Fluidized bed can be used to depolymerize the PBd the PBd is one of several components in the tire. Ozone treatment or ultrasound treatment of rubber tires can be used to remove the sulfur cross-links. Devulcanization is anessential pre-treatment step. The Gas-Liquid-Solid Fluidized bed can be operated at vacuum pressures. Optimal temperature and pressure in the presence of a catalyst such as AlCl$_3$ needs to be arrived at by experimentation.

Method II A dipolar aprotic solvent such as N-Methyl-2-Pyrrolidone or γ-butyrolactone can be used to extract the carbonaceous matter in the waste tires. Similar extraction of bituminous West Virginia coals was reported earlier [40]. The solvent is recovered using water. The recovered Pbd can be re-vulcanized and retreated Techno-economic analysis can be used in order to evaluate the process by method I and the process by method II against the current pyrolysis and incineration methods. Information from mathematical state-space modeling of depolymerization using computers is useful in process design and optimization of yield of the valuable material in the tires. The dynamics of the intermediate product formation is studied in more detail below.
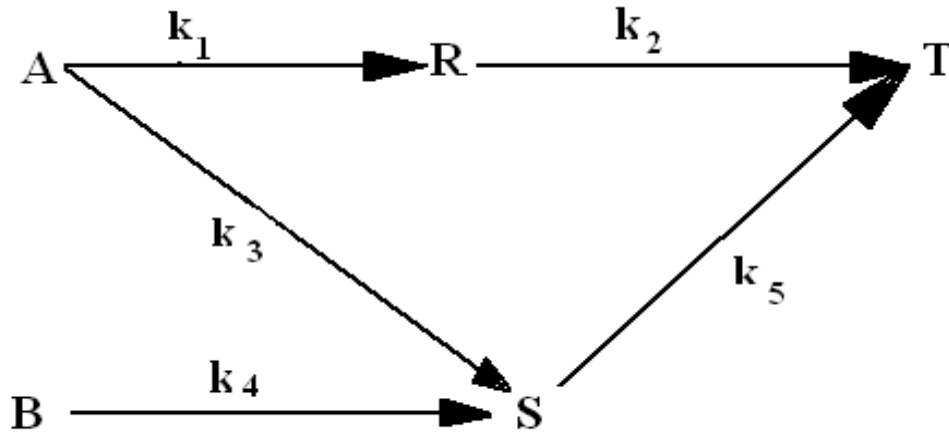
III. Denbeigh Scheme of Reactions

Figure 1.0 : Denbigh Scheme of Reactions

Consider the Denbigh scheme of reactions [41] performed in the CSTR shown in Figure 4.0. A scheme of reactions as shown in Figure 1.0 was discussed in [38] as a special case of Denbeigh reactions. A state space model that can be developed to describe the dynamics of the 5 species, C_A, C_R, C_T, C_B and C_S. The assumptions are that the inlet stream contains species A and B at a concentration of C_{Ai} and C_{Bi} and the initial concentrations of the other species are zero. The kinetics of the simple irreversible reactions shown in Figure 4.0 can be written as follows;

$$\frac{dC_A}{dt} = -(k_1 + k_3)C_A \qquad (4)$$

$$\frac{dC_B}{dt} = -k_4 C_B \qquad (5)$$

$$\frac{dC_S}{dt} = k_4 C_B + k_3 C_A - k_5 C_S \qquad (6)$$

$$\frac{dC_T}{dt} = k_2 C_R + k_5 C_S \qquad (8)$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R \qquad (7)$$
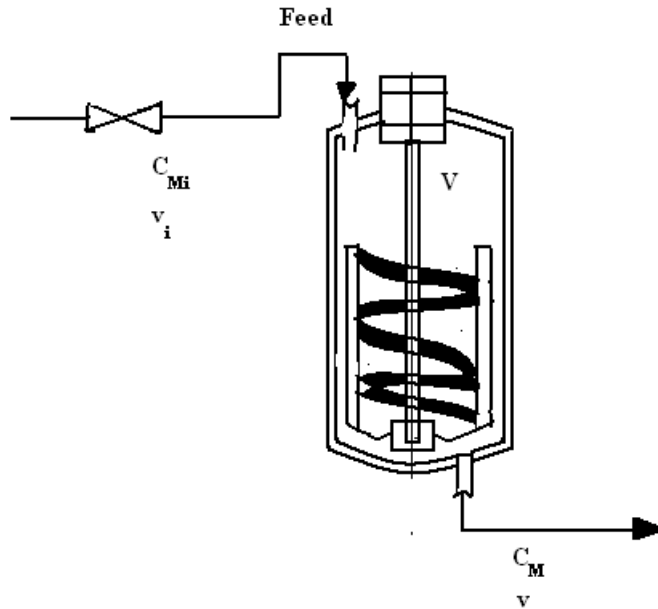

Figure 2.0 : CSTR, Continuous Stirred Tank Reactor

The reactions are considered to peformed in the CSTR similar to the one shown in Figure 2.0. Component mass balances on each of the species assuming incompressible flow and constant volume reactor can be written as follows;

Species A

$$C_{Ai} - C_A(1 + Da_1 + Da_3) = \frac{dC_A}{d\tau} \qquad (9)$$

Where; $Da_1 = k_1\theta; Da_3 = k_3\theta; \tau = \dfrac{t}{\theta}; \theta = \dfrac{V}{v},$ θ with

units of (hr) is the residence time of the species in the reactor, V is the volume of the reactor, (liter) and v is the volumetric flow rate (lit.hr^{-1}) in and out of the reactor.

Species B

$$C_{Bi} - C_B(1 + Da_4) = \frac{dC_B}{d\tau} \qquad (10)$$

Where $Da_4 = (k_4\theta)$

Species S

$$-C_S(1 + Da_5) + Da_4 C_B + Da_3 C_A = \frac{dC_S}{d\tau} \qquad (11)$$

Species R

$$-C_R(1 + Da_2) + Da_1 C_A = \frac{dC_R}{d\tau} \qquad (12)$$

Species T

$$-C_T + Da_2 C_R + Da_5 C_S = \frac{dC_T}{d\tau} \qquad (13)$$

The model equations that can be used to describe the dynamics of the 5 reactant/product species in a CSTR can be written in the state space form as follows;

$$\frac{d}{dt}\begin{pmatrix} C_A \\ C_B \\ C_S \\ C_R \\ C_T \end{pmatrix} = \begin{pmatrix} -(1+Da_1+Da_3) & 0 & 0 & 0 & 0 \\ 0 & -(1+Da_4) & 0 & 0 & 0 \\ Da_3 & Da_4 & -(1+Da_5) & 0 & 0 \\ Da_1 & 0 & 0 & -(1+Da_2) & 0 \\ 0 & 0 & Da_5 & Da_2 & -1 \end{pmatrix}\begin{pmatrix} C_A \\ C_B \\ C_S \\ C_R \\ C_T \end{pmatrix} + \begin{pmatrix} C_{Ai} \\ C_{Bi} \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{14}$$

The stability of the dynamics of the 5 reactants/products in the Denbigh scheme performed a CSTR can be studied by obtaining the eigenvalues of the rate matrix. The characteristic equation for the eigenvalues are obtained by evaluation of the following determinant;

$$\det \begin{pmatrix} (\lambda+1+Da_1+Da_3) & 0 & 0 & 0 & 0 \\ 0 & (\lambda+1+Da_4) & 0 & 0 & 0 \\ Da_3 & Da_4 & (\lambda+1+Da_5) & 0 & 0 \\ Da_1 & 0 & 0 & (\lambda+1+Da_2) & 0 \\ 0 & & Da_5 & Da_2 & (\lambda+1) \end{pmatrix}$$

$$(\lambda+1+Da_1+Da_3)(\lambda+1+Da_4)(\lambda+1+Da_5)(\lambda+1+Da_2)(\lambda+1)=0 \tag{15}$$

The 5 eigenvalues are negative when Damkohler numbers are greater than zero. When eigenvalues are all negative the system is considered to be stable.

The Laplace transform of the model equations developed in order to describe the transient dynamics (Eqs. 39 – 43) for the 5 species in the Denbigh scheme in a CSTR can be written as follows;

$$C_A(s) = \frac{C_{Ai}}{(s)(s+1+Da_1+Da_3)} \tag{16}$$

$$C_B(s) = \frac{C_{Bi}}{(s)(s+1+Da_4)} \tag{17}$$

$$C_S(s) = \frac{Da_3 C_{Ai}}{(s)\left(s+1+Da_1+Da_3\right)(s+1+Da_5)} + \frac{Da_4 C_{Bi}}{(s)(s+1+Da_4)(s+1+Da_5)} \tag{18}$$

$$C_R(s) = \frac{Da_1 C_{Ai}}{(s+1+Da_2)(s)(s+1+Da_1+Da_3)} \tag{19}$$

$$C_T(s) = \left(\frac{1}{s(s+1)}\right)\left(\frac{Da_5 Da_3 C_{Ai}}{(s+1+Da_1+Da_3)(s+1+Da_5)} + \frac{Da_4 Da_5 C_{Bi}}{(s+1+Da_4)(s+1+Da_5)} + \frac{Da_1 Da_2 C_{Ai}}{(s+1+Da_2)(s+1+Da_1+Da_3)}\right)$$

$$\tag{20}$$

The inverse Laplace transform of Eq. (42) can be obtained by invocation of the convolution theorem and written as;

$$\frac{C_A(t)}{C_{Ai}} = \left(\frac{1}{1+Da_1+Da_3}\right)\left(1-e^{-\tau(1+Da_1+Da_3)}\right) \tag{21}$$

The inverse Laplace transform of Eq. (47) can be seen from the time shift property to be;

$$\frac{C_B(t)}{C_{Bi}} = \left(\frac{1}{1+Da_4}\right)\left(1-e^{-(1+Da_4)\tau}\right) \tag{22}$$

The inverse Laplace transform of Eq. (48) can be obtained by look-up of Laplace inversion Tables in Mickley, Sherwood and Reed [42]

$$\frac{C_R(t)}{C_{Ai}} = \frac{\left(e^{-\tau(1+Da_2)}\right)}{(1+Da_2)(Da_2 - Da_1 + Da_3)} - \frac{\left(-e^{-\tau(1+Da_1+Da_3)}\right)}{(1+Da_1+Da_3)(Da_2 - Da_1 - Da_3)} + \frac{1}{(1+Da_2)(1+Da_1+Da_3)}$$

(23)

IV. State Space Representation

State space models are those that describe more than one variable at a given instant in time. Vector form for several variables is used. A set of n differential equations is represented by one equation in matrices and vectors. The coefficient matrix and input and output vectors are used. Output vector can be solved for by matrix manipulations. This would form the output response of the system. The stability of the system can be studied by looking at the Eigen values of the coefficient of the matrix. The different instabilities that may arise and the conditions under which they would arise are given in Table 1.0 [43].

Eigen Values	Characterization of Stability	Stability Type
$\lambda_2 < \lambda_1 < 0$	Asymptotically Stable	Improper Node
$\lambda_2 > \lambda_1 > 0$	Unstable	Improper Node
$\lambda_2 = \lambda_1 = \lambda$	Asymptotically Stable if $\lambda < 0$, Unstable if $\lambda > 0$	Proper or Improper Node
$\lambda_1 < 0 < \lambda$	Unstable	Saddle Point
$\lambda = a \pm ib$	Stable if $a < 0$ Unstable if $a > 0$	Focus or Spiral
$\lambda = \pm ib$	Marginally Stable	Center

Table 1.0 : Characterization of Stability Types

V. Kinetics of Simultaneous Reactions in State Space Form

As an example a state space model is developed to describe the kinetics of the following set of reactions in series and in parallel as suggested in Levenspiel [41]:
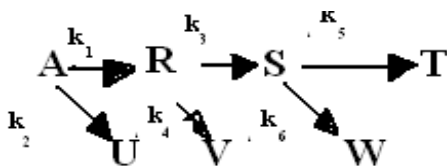

Figure 3.0 : Scheme of 7 Simultaneous Reactions

The kinetics of the 7 simultaneous reactions shown in Figure 3.0 is given below as follows;

$$\frac{dC_A}{dt} = -k_1 C_A - k_2 C_A \qquad (24)$$

$$\frac{dC_R}{dt} = k_1 C_A - k_3 C_R - k_4 C_R \qquad (25)$$

$$\frac{dC_S}{dt} = k_3 C_R - k_5 C_S - k_6 C_S \qquad (26)$$

$$\frac{dC_T}{dt} = k_5 C_S \qquad (27)$$

$$\frac{dC_U}{dt} = k_2 C_A \qquad (28)$$

$$\frac{dC_V}{dt} = k_4 C_R \qquad (29)$$

$$\frac{dC_W}{dt} = k_6 C_S \qquad (30)$$

The above equations can be represented in the state space form in one line as follows;

$$\frac{d}{dt}\begin{pmatrix} C_A \\ C_R \\ C_S \\ C_T \\ C_U \\ C_V \\ C_W \end{pmatrix} = \begin{pmatrix} -(k_1+k_2) & 0 & 0 & 0 & 0 & 0 & 0 \\ k_1 & -(k_3+k_4) & 0 & 0 & 0 & 0 & 0 \\ 0 & k_3 & -(k_5+k_6) & 0 & 0 & 0 & 0 \\ 0 & 0 & k_5 & 0 & 0 & 0 & 0 \\ k_2 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & k_6 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} C_A \\ C_R \\ C_S \\ C_T \\ C_U \\ C_V \\ C_W \end{pmatrix}$$

(31)

Or,

$$\frac{dC}{dt} = KxC$$

(32)

The stability of the system of reactions can be studied by obtaining the Eigen values of the K matrix. The Eigenvalues of the K matrix are obtained from the roots of the characteristic polynomial

$$Det(\lambda I - K) = 0$$

(33)

The K matrix is *sparse*. The polynomial form of the characteristic equation can be written as follows;

$$(\lambda + k_1 + k_2)(\lambda + k_3 + k_4)(\lambda + k_5 + k_6)\lambda^4 = 0$$

(34)

The 7 Eigenvalues are 0 repeated 4 time and $-(k_1+k_2)$, $-(k_3+k_4)$ and $-(k_5 + k_6)$. This system can be viewed as an *integrating system* since all but Eigen values are negative with 4 Eigen values 0.

VI. CONCLUSIONS

As the total energy required to make 1-3 butadiene monomer (60,000 BTU per pound) is greater than the fuel energy value of tire (15,000 BTU per pound), it would be more profitable to recover the butadiene from the waste tires rather than salvaging the fuel value in the waste tires. Furthermore, the stockpiles of was tires cause spread of waste nile virus and cause pandemic. Thermodynamic analysis including P-T phase behviour and the depolymerizationequilibria for polybutadiene has been completed using desktop computers. Different Equation of states such as (i) Tait equation, FOV, Flory Orwoll and Vrij Theory, Prigogine Square-Well cell model, lattice fluid theory of Sanchez and Lacombe were used in the simulations. The Clapeyron equation was derived for ceiling temperature variation with pressure for polybutadiene. Process analysis for two methods for value recovery from waste tires has been drafted. One method is by devulcanization and depolymerization conducted in a three phase fluidized bed. The other method is by swelling and solubilization. A critical step in the reaction process is the optimization of intermediate yield. The dynamics of the general scheme of Denbigh reactions is discussed in detail. State space representation of the series-parallel reactions and criteria for stability are discussed.

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