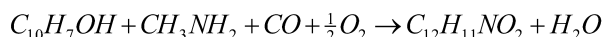


# Oxy-carbonylation reaction path synthesis and its conceptual process design for manufacturing the pesticide Carbaryl

Hsi-Jen Chen\*, Chiu-Hui Dai and Chuan-Yau Chang  
 Department of Chemical and Materials Engineering  
 Tamkang University  
 Tamsui Dist., New Taipei City 25137, TAIWAN  
 e-mail: hjchen@mail.tku.edu.tw

**Abstract**—Four issues in green chemistry are a search for: (1) alternative feedstocks, (2) green solvents, (3) new synthesis pathways, and (4) inherently safer chemistry. In this paper, we propose a novel synthesis pathway to the production of Carbaryl that avoids hazardous intermediates and hazardous by-products by way of an addition reaction, which is considered as one of the atom-economic reactions. This is accomplished by using  $\alpha$ -naphthol, methyl amine, carbon monoxide and oxygen (that is, oxy-carbonylation) as raw materials,



This approach appears to be an excellent synthesis route to produce Carbaryl, with only water as by-product. In the research, we also present all possible synthesis pathways of Carbaryl. The thermodynamic constraints in regard to spontaneity as well as atom economy and safety were provided. In order to extend the green chemistry to green engineering, we also propose a conceptual process design scheme for the manufacture of Carbaryl.

**Keywords**—Green Chemistry; Green Engineering; Atom Economy; Conceptual Process Design; Oxy-carbonylation; Carbaryl.

## I. INTRODUCTION

Carbaryl (1-naphthyl methylcarbamate) is a chemical in the carbamate family used chiefly as an insecticide. It is a white crystalline solid commonly sold under the brand name Sevin, a trademark of the Bayer Company. Union Carbide discovered carbaryl and introduced it commercially in 1958. Bayer purchased Aventis CropScience in 2002, a company that included Union Carbide pesticide operations. It remains the third most-utilized insecticide in the United States for home gardens, commercial agriculture, and forestry and rangeland protection. Approximately 11 million kilograms were applied to U.S. farm crops in 1976 [1]. In 1984 the chemical industry's worst ever disaster occurred at the Union Carbide works in the Indian city of Bhopal. The catastrophe happened at a plant that was used for making the insecticide Carbaryl, which is active against a very wide range of insect pests and is therefore used to protect many fruit and vegetable crops. The reaction routes

are quite hazardous since they involve highly toxic gases, i.e. phosgene and methyl isocyanate (MIC), with TLV-TWA of 0.1 ppm and 0.02 ppm, respectively. Phosgene ( $COCl_2$ ) is one of the most toxic chemicals known. It was used as mustard gas in World War I. Currently, phosgene is used as a raw material in the manufacture of pesticides and urethanes. The traditional methods for manufacturing Carbaryl are illustrated in Fig. 1.

## II. PRINCIPLES OF GREEN CHEMISTRY

Like the Hippocratic Oath to the medical doctors, the "Twelve Principles of Green Chemistry" to the chemists include [2,3]:

1. Prevention—It is better to prevent waste than to treat or clean up waste after it is formed.
2. Atom Economy—Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

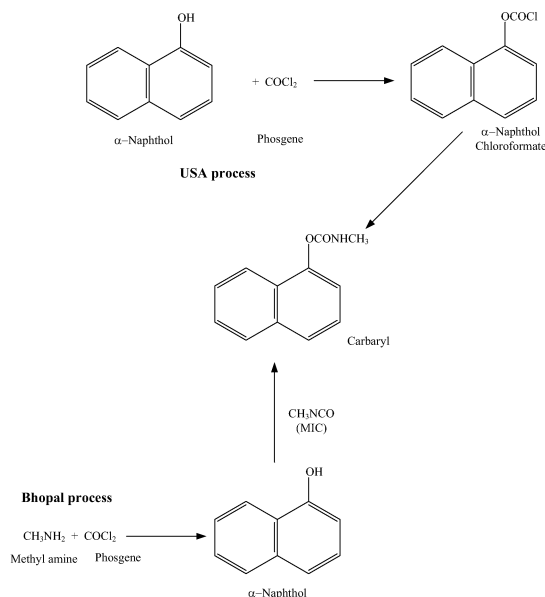


Figure 1. The traditional methods for manufacturing Carbaryl.

3. Less Hazardous Chemical Synthesis—Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals—Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. Safer Solvents and Auxiliaries—The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

6. Design for Energy Efficiency—Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks—A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.

8. Reduce Derivatives—Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalysis—Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation—Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Real-time Analysis for Pollution Prevention—Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention—Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

### III. REACTION PATH SYNTHESIS

Bearing in mind with the main principles of green chemistry, possible reactants and products for producing Carbaryl include [4,5]:

$\text{H}_3\text{C-NH}_2$  (methyl amine),  $\text{HCO-NH-CH}_3$  (N-methyl formamide),  $\text{Cl}_2\text{C=O}$  (phosgene),  $\text{CH}_3\text{-N=C=O}$  (methyl isocyanate),  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{HCl}$  and  $\text{H}_2\text{O}$ .

In order to utilize the oxy-carbonylation reaction, it is necessary to add CO on the reactant list in the study. Therefore, the chemical reaction stoichiometry [6] in previous works and in the present study are summarized in Table 1 and Table 2, respectively.

Table 1. Stoichiometric matrix in previous works

Species \ Elements	C	H	N	O	Cl
$\text{O}_2$	0	0	0	2	0
$\text{H}_2$	0	2	0	0	0
$\text{HCl}$	0	1	0	0	1
$\text{C}_{11}\text{H}_7\text{O}_2\text{Cl}$	11	7	0	2	1
$\text{C}_2\text{H}_5\text{NO}$	2	5	1	1	0
$\text{H}_2\text{O}$	0	2	0	1	0
$\text{CH}_3\text{N}$ (Methyl Amine)	1	5	1	0	0
$\text{COCl}_2$ (Phosgene)	1	0	1	0	2
$\text{C}_2\text{H}_3\text{NO}$ (MIC)	2	3	1	1	0
$\text{C}_{10}\text{H}_8\text{O}$ ( $\alpha$ -Naphthol)	10	8	0	1	0
$\text{C}_{12}\text{H}_{11}\text{NO}_2$ (Carbaryl)	12	11	1	2	0

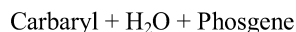
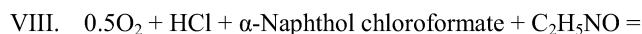
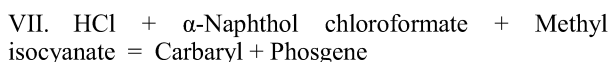
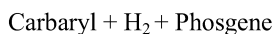
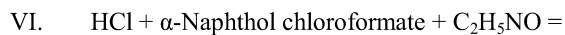
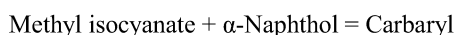
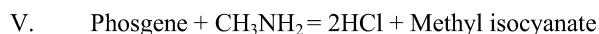
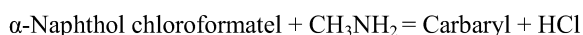
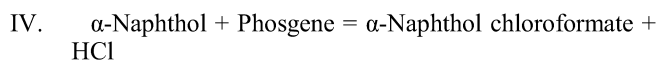
In addition,

Table 2. Stoichiometric matrix in this work

Species \ Elements	C	H	N	O
$\text{O}_2$	0	0	0	2
$\text{H}_2\text{O}$	0	2	0	1
$\text{CH}_3\text{N}$	1	5	1	0
$\text{CO}$	1	0	0	1
$\text{C}_{10}\text{H}_8\text{O}$	10	8	0	1
$\text{C}_{12}\text{H}_{11}\text{NO}_2$	12	11	1	2

As a result, the following possible reaction routes are obtained:

- I.  $\text{CH}_3\text{NH}_2 + \alpha\text{-Naphthol} + \text{CO} + 0.5\text{O}_2 = \text{Carbaryl} + \text{H}_2\text{O}$
- II.  $\text{C}_2\text{H}_5\text{NO} + \alpha\text{-Naphthol} = \text{Carbaryl} + \text{H}_2$
- III.  $0.5\text{O}_2 + \text{C}_2\text{H}_5\text{NO} + \alpha\text{-Naphthol} = \text{Carbaryl} + \text{H}_2\text{O}$



Note that only the first three are non-phosgene. The eight reaction synthesis pathways for making the insecticide Carbaryl is shown in Fig. 2.

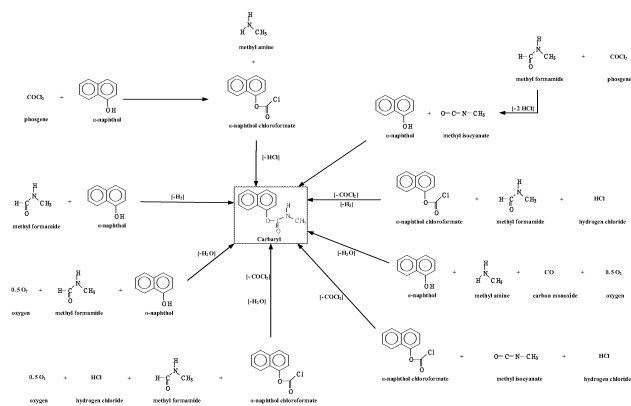


Figure 2. The eight reaction synthesis pathways for manufacturing Carbaryl

#### IV. ATOM ECONOMY

Atom economy, a ratio of the molecular weight of the starting materials and reagents and the molecular weight of the target molecule, provides a measure of the intrinsic efficiency of the transformation [7,8]. Let us take the oxy-carbonylation reaction synthesis pathway for instance,



$$\text{Carbon: } [12/(1+10+1)] \times 100\% = 100\%$$

$$\text{Hydrogen: } [11/(5+8)] \times 100\% = 84.6\%$$

$$\text{Oxygen: } [2/(1+1+1)] \times 100\% = 67\%$$

Mass Efficiency (basis 1 mole of product):

$$\text{Mass in Product} = (12\text{C}) \times (12) + (11\text{H}) \times (1) + (2\text{O}) \times (16) + (1\text{N}) \times 14 = 201 \text{ g}$$

$$\text{Mass in Reactants} = (12\text{C}) \times (12) + (13\text{H}) \times (1) + (3\text{O}) \times (16) + (1\text{N}) \times 14 = 219 \text{ g}$$

$$\text{Mass Efficiency} = \frac{201}{219} \times 100\% = 92\%$$

#### V. SPONTANEITY OF THE REACTION PATH SYNTHESIS

From the perspective of thermodynamics, the spontaneity of the eight reaction routes can be calculated by using the data outlined in Table 3.

Table 3. Species data

Species	Name	Molecular Formula	$\Delta H_{298}^\circ$ (kJ/mol)	$\Delta G_{298}^\circ$ (kJ/mol)	M.W.
1	Oxygen	$\text{O}_2$	0	0	16
2	Hydrogen	$\text{H}_2$	0	0	2
3	Hydrogen Chloride	HCl	-92.4	-95.3	36.5
4	Carbon Monoxide	CO	-270	-92.4	28
5	$\alpha$ -Naphthol Chloroformate	$\text{C}_{11}\text{H}_7\text{O}_2\text{Cl}$	-187	-71	206
6	Methyl Formamide	$\text{C}_2\text{H}_5\text{NO}$	-184	-44	59
7	Water	$\text{H}_2\text{O}$	-242	-237	18
8	Methyl Amine	$\text{CH}_3\text{N}$	-23	320	31
9	Phosgene	$\text{COCl}_2$	-221	-205	91
10	Methyl Isocyanate (MIC)	$\text{C}_2\text{H}_3\text{NO}$	-898	0	57
11	$\alpha$ -Naphthol	$\text{C}_{10}\text{H}_8\text{O}$	-25.5	98	144
12	1-Naphthol-N-Methyl Carbamate (Carbaryl)	$\text{C}_{12}\text{H}_{11}\text{NO}_2$	141	38.5	199

Under the condition of 298 K and 1 bar, reaction pathways I, III, IV and V are spontaneous, II, VI and VIII are non-spontaneous. Reaction pathway VII can be considered as reversible.

#### VI. GREEN ENGINEERING

To extend our study from green chemistry to green engineering. That is, to aim at the production of Carbaryl on a large scale, we first propose our conceptual process design idea in Figure 3. A preliminary block flow diagram is sketched in Figure 4.

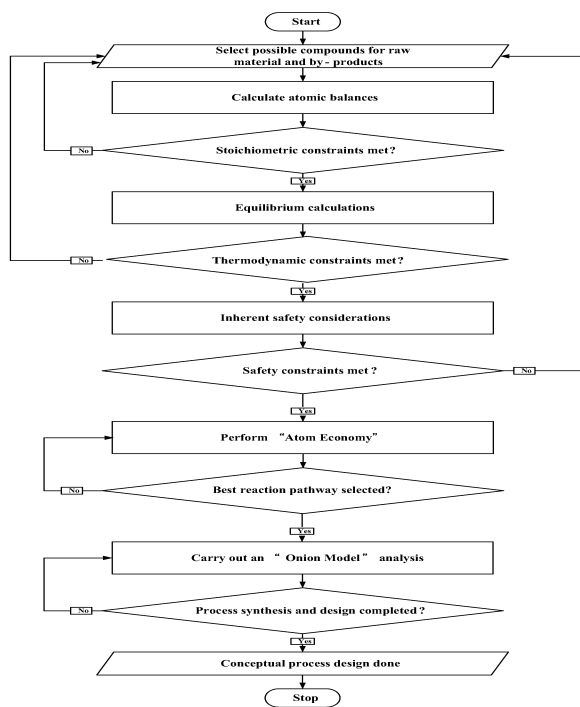


Figure 3. The algorithm for the production of Carbaryl.

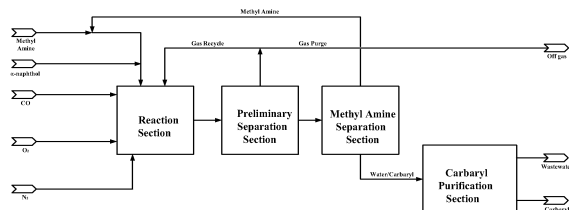


Figure 4. Block flow diagram for the production of Carbaryl.

## VII. REACTION YIELD AND REACTOR SAFETY OF THE OXY-CARBONYLATION SYNTHESIS PATH

Carbaryl is a white crystalline solid with a melting point of 142°C and a density of 1.23 g/cm<sup>3</sup>. Its vapor pressure is low and solubility in water is also very low. The reactor feed consists of  $\alpha$ -naphthol, methyl amine, carbon monoxide, oxygen, and nitrogen as well. Note that nitrogen is added as an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC). Also, in order to optimize the reactor yield, it is necessary to explore the design specifications for the reactor. This is accomplished by using a nonlinear programming (NLP). Under chemical and phase equilibrium, we usually minimize the Gibbs free energy subject to the atom balance constraints to obtain the product distribution of possible reactions. Mathematically, at a given temperature (T) and pressure (P), to calculate the equilibrium mole numbers of the chemical species in the different phases, the Gibbs free energy is minimized subject to the atom balances by summing over all of the possible species in all of the phases.

$$G\{\underline{n}\} = \sum_{j=1}^s \bar{G}_j^c n_j^c + \sum_{\ell=1}^p \sum_{s+1}^c \bar{G}_{j\ell} n_{j\ell} \quad (1)$$

where  $G$  is the total Gibbs free energy,  $\bar{G}_j^c$  is the partial molal Gibbs free energy in pure solid  $j$  ( $c$  denotes a condensed phase),  $\bar{G}_{j\ell}$  is the partial molal Gibbs free energy of species  $j$  in solution phase  $\ell$ , and  $n_j^c$  and  $n_{j\ell}$  are the corresponding mole numbers, with  $\underline{n}$  denoting the vector of these mole numbers. Furthermore, the partial molal Gibbs free energies are expressed as

$$\bar{G}_j = G_j^0 \quad j = 1, \dots, s \quad (2)$$

and

$$\bar{G}_{j\ell} = G_{j\ell}^0 + RT \ln \frac{f_{j\ell}}{f_{j\ell}^0} \quad j = s+1, \dots, c \quad (3)$$

$G_j^0$  and  $G_{j\ell}^0$  are the Gibbs free energies of formation of species  $j$  in the solution phase  $\ell$ , respectively.  $f_{j\ell}^0$  is the fugacity of species  $j$  in phase  $\ell$  in its standard state, and  $f_{j\ell}$  is the mixture fugacity of species  $j$  in phase  $\ell$ .

Substituting Eqs. (2) and (3) in Eq. (1), and adding the atom balance, the following nonlinear program is obtained:

$$\text{Minimize: } G = \sum_{j=1}^s G_j^0 n_j^c + \sum_{\ell=1}^p \sum_{j=s+1}^c n_{j\ell} (G_{j\ell}^0 + RT \ln \frac{f_{j\ell}}{f_{j\ell}^0}) \quad (4)$$

$$\text{Subject to: } b_k = \sum_{j=1}^s m_{jk} n_j^c + \sum_{\ell=1}^p \sum_{j=s+1}^c m_{jk} n_{j\ell} \quad k = 1, \dots, E$$

where  $b_k$  is the gram-atoms of element  $k$ ,  $E$  is the total number of elements, and  $m_{jk}$  is the number of atoms of element  $k$  in species  $j$ . Equation (4) is then solved using common optimization methods.

By adding nitrogen to the packed bed reactor of the oxy-carbonylation synthesis process, the feed should lie outside the explosive (flammability) limits. For mixtures of gases, the following equations are used to predict the mixture flammability limits:

$$LFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{LFL_i}}, \quad UFL_{mix} = \frac{1}{\sum_{i=1}^n \frac{y_i}{UFL_i}} \quad (5)$$

where  $LFL_i$  and  $UFL_i$  are the lower and upper flammability limits for component  $i$  in volume (mole) % of component  $i$  in fuel and air,  $y_i$  is the mole fraction of component  $i$  on a combustible basis, and  $n$  is the number of combustible species. Indeed, nowhere in the packed bed reactor should the composition lie within the explosive limits. Operation outside these limits can be accomplished by diluting the feed with an inert gas such as nitrogen. The above calculations for LFL

and UFL are based strictly on mixtures of fuel and air only. When an inert material is used, Eq. (5) must be changed. The easiest way to do this is to compute the LOC which can be calculated as follows:

$$LOC = LFL_{mix} \left( \frac{\text{moles of oxygen for complete combustion}}{\text{moles of hydrocarbons}} \right) \quad (6)$$

If the inlet concentration of oxygen to the reactor is lower than the LOC, then the mixture is non-explosive.

#### VIII. PROCESS FLOW DIAGRAM FOR THE PRODUCTION OF CARBARYL

Combining the block flow diagram (Fig. 4) and heuristics of process synthesis [9], we are able to present the process flow diagram for the production of Carbaryl as shown in Fig. 5. Note that switch condensers, shown as Cond-101 and Cond-102, are used.

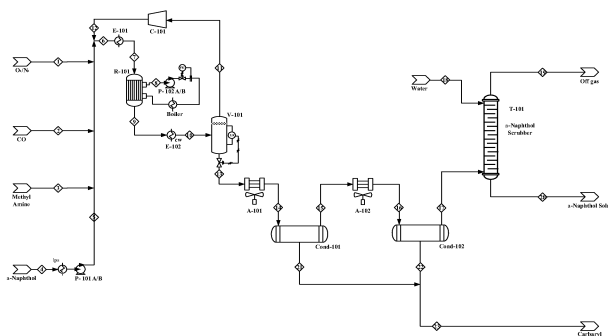


Figure 5. Preliminary process flow diagram for the production of Carbaryl.

#### IX. CONCLUSION

In this work, we have proposed a new, non-phosgene reaction route to the production of Carbaryl by using  $\alpha$ -naphthol, methyl amine, carbon monoxide and oxygen (that is, oxy-carbonylation) as raw materials. This approach appears to be an excellent synthesis pathway to produce Carbaryl, with only water as by-product. Our current work focuses on the process design and integration for the making of the insecticide Carbaryl. This research may provide a valuable reference for sustainable processes.

#### REFERENCES

- [1] Metcalf, R. L. (2002). Insect Control in Ullmann's encyclopedia of industrial chemistry. Wiley-VCH, Weinheim, Germany.
- [2] Anastas, P.T., & Warner, J.C. (1998). Green chemistry theory and practice. Oxford University Press, New York, U.S.A.
- [3] Lancaster, M. (2002). Green chemistry an introductory text. Royal Society of Chemistry, Cambridge, U.K.
- [4] Crabtree, E.W., & El-Halwagi, M.M. (1994). Synthesis of environmentally acceptable reactions. Pollution prevention via process and product modifications. AIChE Symposium Series 90, 117-127.
- [5] Buxton, A., Livingston, A.G., & Pistikopoulos, E.N. (1997). Reaction path synthesis for environmental impact minimization. Computers and Chemical Engineering, 21, Suppl. S959-S964.
- [6] Smith, W., & Missen, R.W. (1982). Chemical reaction equilibrium analysis. John Wiley and Sons, Inc., New York, U.S.A.
- [7] Trost, B.M. (1991). The atom economy—a search for synthetic efficiency. Science, 254, 1471-2477.
- [8] Allen, D.T., & Shonnard, D.R. (2002). Green engineering: environmentally conscious design of chemical processes, Prentice-Hall, Inc. New Jersey, U.S.A.
- [9] Seider, W., Seader J.D., & Lewin, D.R. (1998). Process design principles synthesis, analysis, and evaluation. John Wiley and Sons, Inc., New York, U.S.A.