SES COLLEGE SREEKANDAPURAM

(Accredited by NAAC with 'B' Grade) Affiliated to Kannur University

Criterion 3
Research,Innovation and Extension

3.3- Research Publication and Awards

3.3.3 Number of books and chapters in edited volumes/books published and papers published in national/ international conference proceedings per teacher during 2020-2021

Green Chemistry and Applications

Editors

Aidé Sáenz-Galindo
Adali Oliva Castañeda Facio
Raúl Rodríguez-Herrera

CRC Press
Taylor & Francis Group
A SCIENCE PUBLISHERS BOOK

Green Chemistry and Applications

Editors
Aidé Sáenz-Galindo
Adali Oliva Castañeda-Facio
School of Chemistry
Autonomous University of Coahuila
Saltillo, Coahuila, México

Raúl Rodríguez-Herrera
Food Research Department
School of Chemistry
Autonomous University of Coahuila
Saltillo, Coahuila, México

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business
A SCIENCE PUBLISHERS BOOK

Cover credit: Cover illustrations reproduced by kind courtesy of the editors.

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2021 by Taylor & Francis Group, LLC

CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Version Date: 20200601

International Standard Book Number-13: 978-0-367-26033-0 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, includ-ing photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Library of Congress Cataloging-in-Publication Data

Names: Sáenz-Galindo, Aidé, 1979- editor. | Facio, Adali Oliva Castañeda, 1978- editor. | Rodríguez-Herrera, Raúl, 1960- editor.
Title: Green chemistry and applications / editors, Aidé Sáenz-Galindo, Adali Oliva Castañeda-Facio, School of Chemistry, Autonomous University of Coahuila, Saltillo, Coahuila, México, Raúl Rodríguez-Herrera, Food Research Department, School of Chemistry, Autonomous University of Coahuila Saltillo, Coahuila, México.
Description: Boca Raton, FL : CRC Press, 2020. | Includes bibliographical references and index.
Identifiers: LCCN 2020000047 | ISBN 9780367260330 (hardcover)
Subjects: LCSH: Green chemistry.
Classification: LCC TP155.2.E58 G725 2020 | DDC 660.028/6--dc23
LC record available at https://lccn.loc.gov/2020000047

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.routledge.com

Chapter 2

Atom Economy

Kunnambeth M. Thulasi[1], Sindhu Thalappan Manikkoth[1],
Manjacheri Kuppadakkath Ranjusha[1],
Padinjare Veetil Salija[1], Vattakkoval Nisha[1],
Shajesh Palantavida[2] and
Baiju Kizhakkekilikoodayil Vijayan[1]*

[1]Department of Chemistry/Nanoscience, Kannur University,
Swami Anandha Theertha Campus, Payyannur, Edat P.O.,
Kerala-670 327, India.
[2]Centre for Nano and Materials Science, Jain University,
Jakkasandra, Ramanagaram, Karnataka, India.

INTRODUCTION

The concept of atom economy was developed by Barry M. Trost in 1991. Organic synthesis requires multiple reagents, facilitating agents and solvents to obtain the desired product. At the end of the reaction everything except for the desired product and reagents that can be recycled, like solvents and catalysts, will end up as wastes, mostly hazardous wastes. Conceptually, if the desired product contains all the atoms making up the reagents there will be no waste generated. The concept of atom economy can be used to identify synthetic methodologies that will retain the maximum number of atoms from the reactants in the final product and thereby reduce wastage. The atom economy concept allows quantification of the efficiency of a reaction with respect to the number of atoms transferred from the reactants to the final desired product (Trost, 1995; Trost, 2002). The concept of atom economy can be applied to every synthesis and be used to define new pollution prevention benchmarks (Cann and Dickneider, 2004; Song et al., 2004). Atom economy calculation, broadly presents a measure of the greenness of a chemical reaction.

---

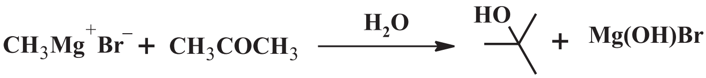
*For Correspondence: baijuvijayan@kannuruniv.ac.in; baijuvijayan@gmail.com

The commonly used indicator for efficiency of a reaction in organic synthesis is the percentage yield, which neglects mass flow (Cann and Dickneider, 2004). A synthetic chemist records the yield of a particular reaction as percentage yield. The percentage yield can be calculated as

$$\%\text{yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

A yield above 90% is considered good.

From the above calculations, it can be understood that if one mole of the reactant produces one mole of the product we get 100% yield. However, the amount of waste produced is not factored in the above calculation. So a synthesis cannot be characterized in terms of greenness, even if it has a 100% yield (Eissen et al., 2004). An example is the Grignard reaction (Scheme 2.1). It cannot be considered green, even though it gives a 100% yield. A large amount of by-products is formed in the reaction.



Scheme 2.1 Grignard reaction.

Here one mole of acetone gives one mole of tert-butyl alcohol. But one mole of Mg(OH)Br is formed as a by-product which is not taken into account while calculating the yield.

Here lies the need for an accurate gauge for the greenness of a chemical reaction and leads to the concept of atom economy. If there are two possible schemes for a synthesis, the one, more consistent with green principles should be chosen. Such a synthetic route, will mainly incorporate the maximum number of atoms from the reagents into the desired final product (Anastas et al., 2002). Hence the concept of atom economy concentrates on developing synthetic schemes that will reduce waste by maximizing the incorporation of atoms from the reactants in the desired product. By following the atom economy one can design greener reactions.

The quantification of atom economy concept was conducted by Roger A Sheldon (Kidwai and Mohan, 2005), a professor at Delft University in the Netherlands. He introduced the percentage atom utilization as a measure of atom economy and is given as

$$\%\ \text{Atom utilization} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of formed product} + \text{Waste product}} \times 100$$

Percentage atom utilization is the percentage of atoms in the reactants that are incorporated into the final product. If more than one product of interest is formed in a reaction, percentage atom utilization equation is modified as

$$\%\ \text{Atom utilization} = \frac{(\Sigma N_p W_p)}{[(\Sigma N_p W_p) + (\Sigma N_r W_r)]} \times 100$$

where,

N_p = Number of molecules of the products
N_r = Number of molecules of the residues
W_p = Formula weight of products
W_r = Formula weight of residues

An example of a 100% atom utilization reaction is the reaction between sodium sulfite and sulfur powder to form sodium thiosulfate, which is given in Scheme 2.2.

$$\mathbf{Na_2SO_3 + Sulfur \longrightarrow Na_2S_2O_3}$$

Scheme 2.2 Formation of sodiumthiosulfate.

In several reactions, it is difficult to determine the identities of waste products and the concept of percentage atom utilization cannot be used. The law of conservation of mass provides a better platform for understanding the maximum inclusion of all the atoms of the reactants in the final products and is applied for calculating percentage atom economy. It is given by:

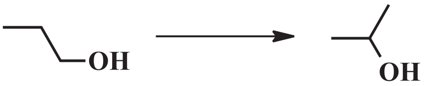
$$\%\ \text{Atom economy} = \frac{\text{formula weight of atoms utilized}}{\text{total formula weight of all the reagents used in this reaction}} \times 100$$

ATOM ECONOMY IN DIFFERENT TYPES OF REACTIONS IN ORGANIC SYNTHESIS

The concept of atom economy can be best understood by considering examples of different kinds of reactions. There are four main types of reactions in organic synthesis; rearrangement, addition, substitution and elimination reactions. By calculating the percentage atom economy, we can find out which one is more atom economical.

Rearrangement Reactions

All rearrangement reactions are carried with 100% atom economy as it involves only the rearrangements of the atoms of a molecule. As an illustration, consider the rearrangement reaction of propan-1-ol to propan-2-ol (Scheme 2.3).



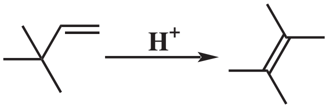
Scheme 2.3 Rearrangement reaction of propan-1-ol to propan-2-ol.

Here all the atoms in the reactant molecule are utilized in the final desired product.

$$\%\ \text{Atom economy} = \frac{\text{formula weight of atoms utilized}}{\text{total formula weight of all the reagents used in this reaction}} \times 100$$

$$= \frac{60}{60} \times 100 = 100\%$$

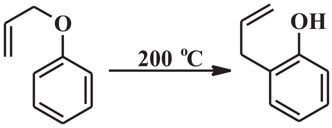
Consider the rearrangement of 3, 3-dimethyl-1-butene to 2, 3-dimethyl-2-butene in presence of acid catalyst (Scheme 2.4).



Scheme 2.4 Rearrangement of 3, 3-dimethyl-1-butene to 2, 3-dimethyl-2-butene in presence of acid catalyst.

$$\%\text{ Atom economy} = \frac{60}{60} \times 100 = 100\%$$

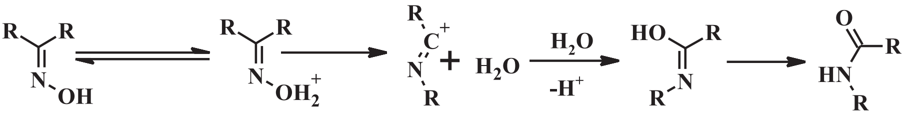
Here also all the atoms in the reactant are rearranged to form the final product and atom economy is found to be 100%. The acid used in the reaction is not included in the calculation because it is only required in catalytic amounts and does not form part of the product. The Claisen rearrangement is another classical example of 100% atom efficiency reaction, which involves rearrangement of aromatic allyl ethers producing ortho-substituted product, is illustrated in Scheme 2.5.



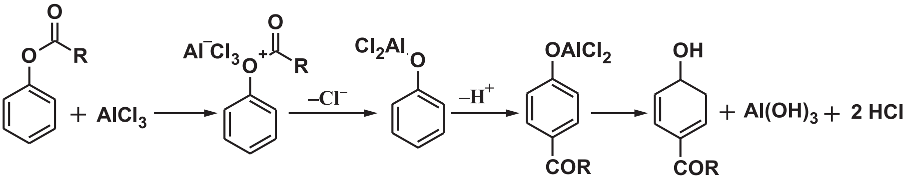
Scheme 2.5 Claisen rearrangement.

$$\%\text{ Atom economy} = \frac{134.75}{134.75} \times 100 = 100\%$$

An important rearrangement involving catalysts is the beckmann reagent where a cyclohexanone oxime converted to caprolactum in the presence of oleum (Scheme 2.6), a major precursor for the synthesis of nylon 6. Fries rearrangement of phenolic esters also go through a catalytic route involving lewis acid such as $AlCl_3$ as catalyst, which is given in Scheme 2.7. However the use of a large amount of catalyst increases the aluminum waste thereby reducing atom efficiency. In order to make it atom economic, photo-fries rearrangement is carried out where the reaction takes place through an intermolecular free radical route.



Scheme 2.6 Beckmann rearrangement.



Scheme 2.7 Fries rearrangement.

Even though rearrangement reactions are considered to show 100% atom economy, there are few exceptions. Some rearrangement reactions involve elimination of water reducing the theoretical atom economy. Similarly, rearrangements involving intermediates along the reaction pathway show less atom economy.

Addition Reactions

Addition reactions are reactions in which there occur an addition of molecules or groups across a double or triple bond. These reactions are 100% atom economical (Trost, 2002), since the reactants combine to form the final product, without any elimination of side products. We can consider an example for addition reaction.

Considering the hydrogenation of ethene (Scheme 2.8), all the atoms of ethene and hydrogen molecule are utilized in forming the final product ethane. Here, nickel is only required in catalytic amounts and will not influence the calculation of atom economy.

$$\mathrm{H_2C{=}CH_2 + H_2 \xrightarrow{Ni} H_3C{-}CH_3}$$

Scheme 2.8 Hydrogenation of ethene.

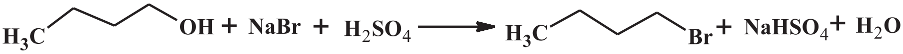
In this reaction, the total formula weight of reagents used is 30 g/mole and the total formula weight of atoms utilized is also 30 g/mole and thus the percentage atom economy is 100%.

Other examples of simple addition reactions include carbonylation, bromination, chlorination, etc. which also proceeds with 100% atom economy. Geier et al. in 2010 reported metal free reductions of N- heterocycles in the presence of a catalytic amount of borane, $B(C_6F_5)_3$ and hydrogen.

Substitution Reactions

Substitution reactions take place by the replacement of one or a group of atoms by another atom or group of atoms. These reactions are usually poor in terms of atom economy.

Consider the example of acid promoted nucleophilic substitution reaction, given in Scheme 2.9.



Scheme 2.9 Bromination of butanol.

Here, some atoms of the reactants are wasted and some are incorporated in the desired products. We can see that half of the mass of the reactants converts to the desired products and the rest is wasted as unwanted materials.

Total formula weight of reagents used = 275 g/mole

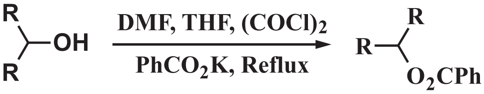
Total formula weight of atoms utilized = 138 g/mole

$$\% \text{ Atom economy} = \frac{\text{formula weight of atoms utilized}}{\text{total formula weight of all the reagents used in this reaction}} \times 100$$

$$= \frac{138}{275} \times 100 = 50\%$$

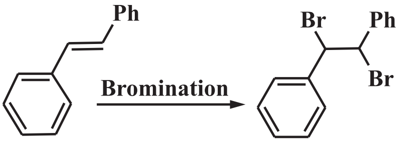
i.e., for the above reaction % atom economy is only 50%.

In the Mitsunobu reaction of conversion of secondary alcohols to ester, diethyl azodicarboxylate and triphenyl phosphine are used as reagents. Diethyl azocarboxylate is unstable and explosive in nature. The byproducts of the reactions also have considerable mass. Therefore the reaction is not ideal and has low atom economy. Instead of these reagents, Barret in 1998 used imidate esters (Barrett et al., 1998), produced from DMF and oxalyl chloride. This, on reaction with potassium benzoate leads to SN_2 substitution reaction of secondary alcohols. This reaction, given in Scheme 2.10 minimizes the quantity of nucleophile which improves atom economy. Moreover, the side products (DMF and KCl) can be removed easily.



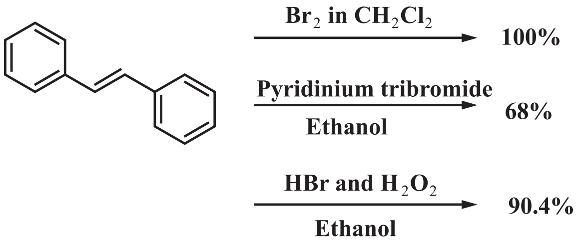
Scheme 2.10 Mitsunobu reaction using imidate esters.

Generally, bromination of alkenes is carried out with liquid bromine in non-reacting or acidic solvents like CH_2Cl_2, CCl_4 and glacial acetic acid. This easy method can be completed in 10 minutes. But the chemicals used are harmful, carcinogenic and a skin irritant. Mckenzie et al. in 2005, utilized pyridiniumtribromide as a bromine source to make this reaction greener. This reaction used ethanol as a solvent instead of glacial acetic acid. Reaction was carried out at room temperature. But a disadvantage was that, the reaction was less atom economical than the classical reaction. Instead of the above mentioned reactants, they used hydrobromic acid in the presence of hydrogen peroxide as a bromine source and high atom economy could be achieved. Consider bromination of Stilbene given in Scheme 2.11.



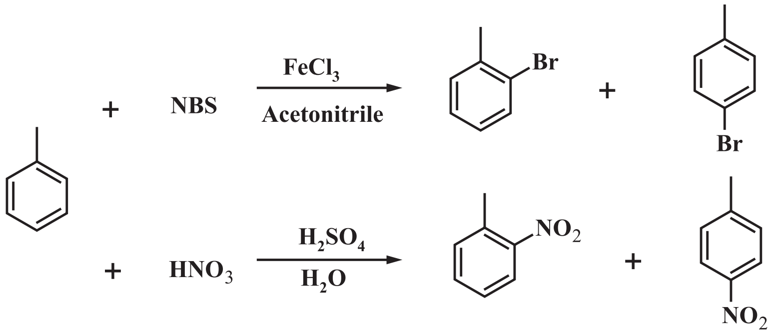
Scheme 2.11 Bromination of stilbene.

In the process stilbene is dissolved in ethanol and heated to reflux. HBr and 30% H_2O_2 are then added to the mix. Orange color appears in the solution, indicating the formation of bromine in the system. The reaction mixture becomes colorless as the product precipitates out. The atom economies of bromination of stilbene in classical and green methods are given in Scheme 2.12.



Scheme 2.12 Atom economies of bromination of stilbene.

Fishback in 2016 compared the aromatic electrophilic substitution (bromination and nitration) reactions of toluene (Fishback et al., 2016). Bromination using N-bromosuccinimide and nitration with nitric acid, illustrated in Scheme 2.13, were chosen for their study.



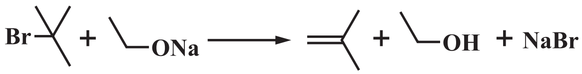
Scheme 2.13 Bromination and nitration of toluene.

Atom economy of nitration reaction is 85% and that of bromination is 63%. Functionalization by nitration reaction is greener than bromine substitution to obtain monosubstituted toluene. Even though nitration is greener from the perspective of atom economy and green principles, it is more difficult to execute than bromination.

Elimination reactions

In the case of elimination reactions, two atoms or group of atoms are lost from the reactant. Therefore, the reaction can never be atom economical. These are considered the worst atom economical reactions among the four.

Consider preparation of methyl propane from 2-bromo 2-methyl propane, given in Scheme 2.14.



Scheme 2.14 Preparation of methyl propane.

Total formula weight of reagents used = 205 g/mole
Total formula weight of atoms utilized = 56 g/mole

$$\% \text{ Atom economy} = \frac{\text{formula weight of atoms utilized}}{\text{total formula weight of all the reagents used in this reaction}} \times 100$$

$$= \frac{56}{205} \times 100 = 27\%$$

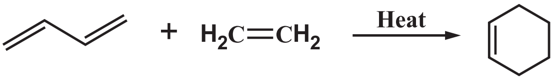
i.e., for the above reaction percentage atom economy is only 27.

There are several other types of reactions, such as pericyclic reactions, carbon-carbon coupling reactions, non carbon-carbon coupling reactions, condensation reactions, redox type reactions, multicomponent reactions, isomerizations, etc. The atom economy of these reactions can also be calculated.

Pericyclic Reactions

Pericyclic reactions are concerted reactions in which reorganization of electrons occur via a single cyclic transition state. There are different types of pericyclic reactions, such as cycloaddition, electrocyclic reaction, sigmatropic rearrangement, group transfer reaction, chelotropic reaction and diatropic rearrangement. Pericyclic reactions are 100% atom economical, like simple addition and rearrangement.

Consider the cycloaddition of butadiene and ethene (Diels-Alder reaction), the product obtained is cyclohexene and takes place in presence of heat, illustrated in Scheme 2.15.



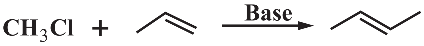
Scheme 2.15 Diels – Alder reaction.

Here the total formula weight of reagents used is 82 g/mole and the total formula weight of atoms utilized is also 82 g/mole giving a percentage atom economy of 100%.

Coupling Reactions

In organic chemistry, the term coupling reaction encompasses a variety of reactions, where 2 reaction fragments join each other by forming new bonds between atoms, with the help of a catalyst. Fischer indole synthesis, Danishefsky synthesis, Meerweinarylation, Kolbe synthesis, Zincke-Suhl synthesis, Robinson annulation, Gattermann-Koch reaction, Henry reaction, Heck reaction, Nazarov cyclization, Stoltz aerobic etherification, Buchwald-Hartwig cross coupling, Stahl aerobic amination, Polonovski reaction, etc. are some named organic reactions belonging to this category.

Consider the Heck reaction between methyl chloride and propene in presence of a base and palladium catalyst to form 2-butene, given in Scheme 2.16.



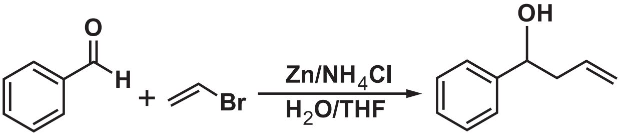
Scheme 2.16 Heck reaction.

Formula weight of all the reactants used = 92.5 g/mole
Formula weight of atoms utilized = 56 g/mole

$$\% \text{ Atom economy} = \frac{56}{92.5} \times 100 = 60.5\%$$

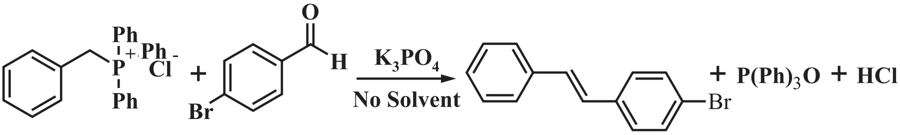
Here the percentage atom economy is only 60.5%.

Fishback et al. in 2016 compared various reactions through a green approach. According to him, the Barbier reaction which is an aqueous version of the Grignard reaction, is less toxic and greener than the Grignard reaction, illustrated in Scheme 2.17. Unlike the Barbier reaction, the Grignard synthesis has to be performed in anhydrous condition in organic solvents. Atom economy of the Barbier reaction is 65%.



Scheme 2.17 Barbier reaction.

Classical Wittig reaction using organic solvents and waste generation is very high. For making it greener, Fishback et al. 2016 proposed a grinding method to induce contact between the reactants in the absence of any solvent (Scheme 2.18). This greener method has an improved atom economy of 45%.

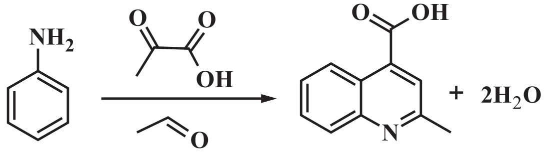


Scheme 2.18 Green wittig reaction.

Multicomponent Reactions

These are a special type of addition reactions in which at least three substrates react together in one reaction vessel either sequentially or all at once (Posner, 1986; Ugi et al., 1994; Dömling, 2002). Here the order of addition of substrates determines the final product of the reaction. Strecker synthesis of R-cyanoamines, Hantzschdihydropyridine synthesis, Radziszewski imidazole synthesis reaction, Riehmquinoline synthesis, Doebner reaction, Pinner triazine synthesis, Hantzsch synthesis, Biginelli reaction, Thiele reaction, etc. belong to the category of multicomponent reactions.

Consider the Doebner reaction of aniline with acetaldehyde and pyruvic acid forming quinolone-4-carboxylic acid (Scheme 2.19).



Scheme 2.19 Doebner reaction.

Formula weight of all the reactants used = 225 g/mole
Formula weight of atoms utilized = 187 g/mole

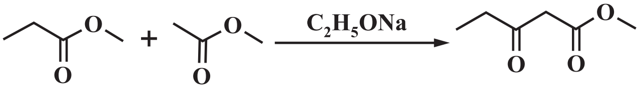
$$\% \text{ Atom economy} = \frac{187}{225} \times 100 = 83.1\%$$

From the calculation here, the percentage atom economy is 83.1%.

Condensation Reactions

Condensations are reactions in which carbon-carbon coupling takes place by straight-chain additions or cyclizations, producing hydroxylic molecules like water or alcohol as a byproduct. Dieckmann condensation, Stobbe condensation, Nenitzescuindole synthesis, Mukaiyamaaldol condensation and acyloin condensation are some examples.

Consider the example of Claisen condensation between methyl propanoate and methyl methanoate, in the presence of the base sodium ethoxide, forming the ketone derivative, with the elimination of ethanol as given in Scheme 2.20.



Scheme 2.20 Claisen condensation.

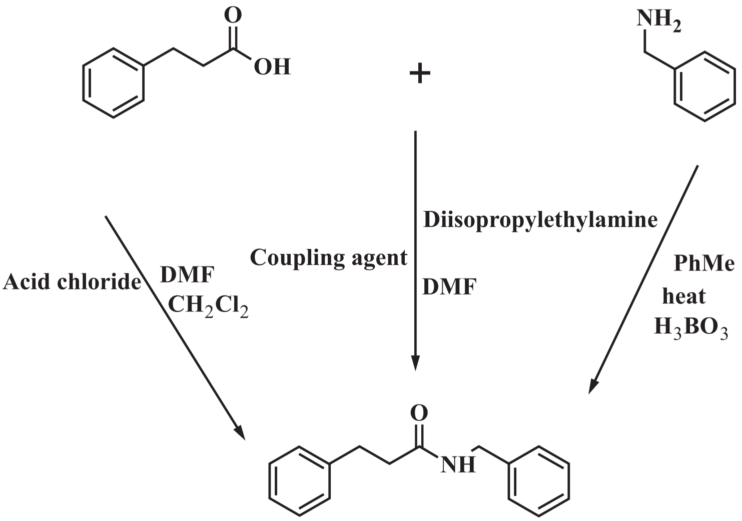
Formula weight of all the reactants used = 162 g/mole
Formula weight of atoms utilized = 130 g/mole

$$\% \text{ Atom economy} = \frac{130}{162} \times 100 = 80.2\%$$

The percentage atom economy is 80.2%.

Amide formation reaction is the most important topic in the area of pharmaceutics. For the preparation of amide bonds, the two classical methods used are acid chloride route and coupling agent method. The first method is the reaction of amine with an acid halide, an acid anhydride or an ester. In the second method, amine reacts with carboxylic acid in the presence of coupling reagents like dicyclohexylcarbodiimide. These methods have the disadvantage of being less safe and having a low atom economy. Fennie in 2016 proposed a catalytic method for the formation of amides involving generation of water as the byproduct, a greener alternative (Fennine and Roth, 2016).

As an example, consider the synthesis of N-benzyl-3-phenylpropanamide using the above three methods, given in Scheme 2.21.



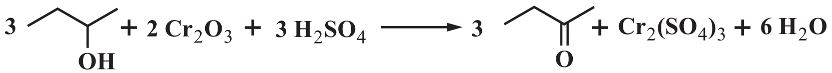
Scheme 2.21 Synthesis of N-benzyl-3-phenylpropanamide through various methods.

A comparison of the atom economy of these three reactions show that the acid chloride route has 49% atom economy, the coupling reagent method has only 31% atom economy and the catalytic method using boric acid catalyst has 93% atom economy. This affirms the greenness of the process along with the low cost.

Redox-type Reactions

Redox-type reactions involve oxidation or reduction of reactants in the presence of oxidizing or reducing agents respectively. These reactions usually produce significant by product wastes mostly from the oxidation or reduction of the reducing and oxidizing reagents (Andaros, 2005a, b; Sipos et al., 2013). Redox type reactions require the presence of another redox couple for converting byproducts back to the initial oxidizing or reducing reagents (Sato, 1998). These reactions are not green in terms of atom economy.

Consider the oxidation of 2- butanol to 2- butanone using the Jone's reagent (Scheme 2.22).



Scheme 2.22 Oxidation using Jone's reagent.

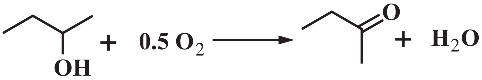
Formula Weight of all the reactants used = 820 g/mole

Formula weight of atoms utilized = 216 g/mole

$$\% \text{ Atom economy} = \frac{820}{216} \times 100 = 26.3\%$$

Cascade redox reactions, resulting in water as the ultimate waste product has recently been developed (Wardman, 1989). Molecular oxygen from air and hydrogen peroxide are the optimal oxidizing agents which produce water as the byproduct (Choudary et al., 2003) and hydrogen gas is the optimal reducing agent which produces no byproducts. Catalytic oxidations are always superior to the above stoichiometric oxidations in the calculation of atom economy.

Consider the above example of oxidation of 2-butanol to 2-butanone, in the presence of oxygen and a catalyst, illustrated in Scheme 2.23.



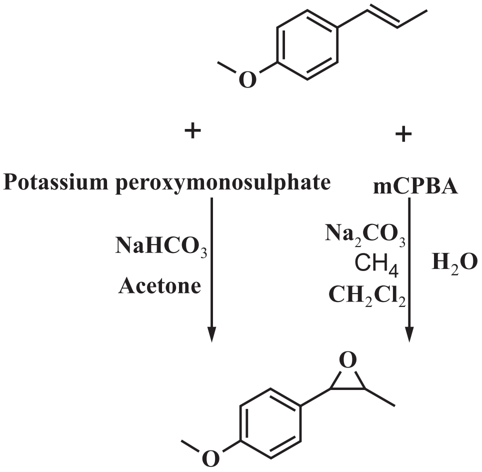
Scheme 2.23 Catalytic oxidation.

Formula weight of all the reactants used = 90 g/mole
Formula weight of atoms utilized = 72 g/mole

$$\%\text{ Atom economy} = \frac{72}{90} \times 100 = 80\%$$

Percentage atom economy is almost three times compared to stoichiometric oxidation.

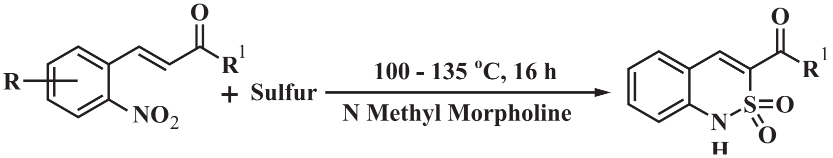
Fishback et al. in 2016, studied epoxidation of trans-Anethole using potassium peroxymonosulfate and meta- Chloroperoxy benzoic acid as oxidizing agents to produce trans - Anethole oxide, illustrated in Scheme 2.24.



Scheme 2.24 Epoxidation of trans-anethole.

The atom economy of epoxidation reaction using mCPBA (51%) is higher as compared to that involving potassium peroxymonosulphate (36%). Epoxidation using mCPBA is also cheaper. Therefore, it is the greener one from the perspective of atom economy and cost consideration.

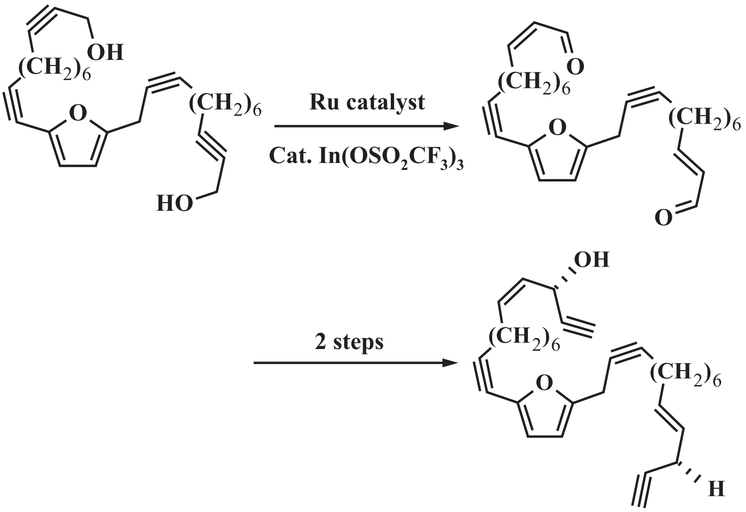
Nguyen and Retailleau in 2017, reported for the first time, a redox-neutral, catalyst free, completely atom-economical synthesis of sultams. Sultams are cyclic derivatives of sulfonamides and are used as important scaffolds in medicinal chemistry. Their uses also include antibacterial activity, lipoxygenase inhibition, drugs for heart disease, etc. Redox and non-redox approaches were widely used for the preparation of sulfonamides and sultams. In the redox method, the widely used strategy is the oxidation of sulfonamide derivatives such as sulfenylamides and sufinylamides and in non-redox method, the condensation of amines with activated sulfonyl group is utilized. In both strategies, the atom economy can never attain 100%. In the new method, elemental sulfur was used as a versatile synthetic tool in sulfonamide synthesis without any byproducts. Nguyen presented a total atom economical approach for the synthesis of sultams (Scheme 2.25) which involves heating of 2-nitrochalcones with elemental sulfur in the presence of N-methylmorpholine or 3-picoline without any catalyst.



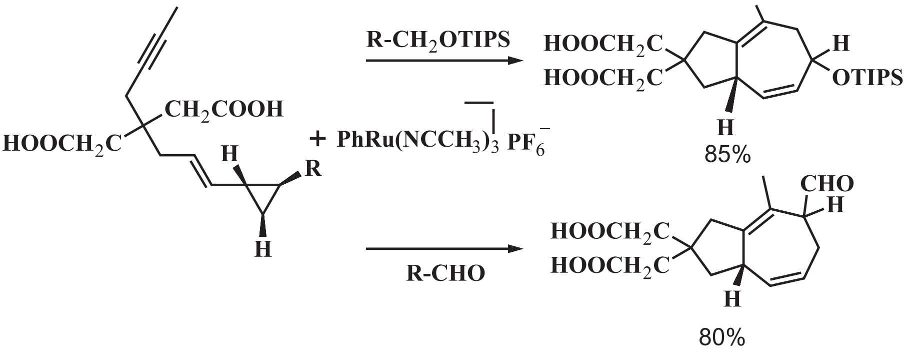
Scheme 2.25 Synthesis of sultams from 2-nitrochalcone.

Isomerizations

Synthesis of conjugated carbonyl compounds by the isomerization of propargyl alcohol represents an atom economical reaction. The isomerization of propargyl alcohols into enones occur via a traditional two step stoichiometric redox reaction in presence of a Ruthenium catalyst. Total synthesis of adociacetylene B through an enantioselective route is shown in Scheme 2.26. Conversion of alkynylvinylcyclopropene to a fused ring structure with ring size 5 or 7 also shows ideal atom economy (Li and Trost, 2008), which is shown in Scheme 2.27.



Scheme 2.26 Isomerization of propargyl alcohol.



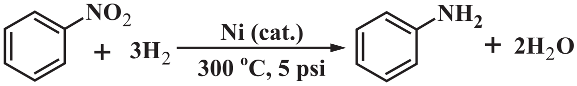
Scheme 2.27 Conversion of alkynylvinylcyclopropene.

ATOM ECONOMY IN CATALYSIS

Catalysis offers atom efficient reactions through an alternative reaction pathway by lowering the activation energy and thereby enhancing the rate of chemical processes. Catalysts can be excluded from the atom economy calculation, as they are not used in the reaction. The use of homogenous, heterogenous or biocatalysts helps to reduce reaction steps, stoichiometric components and energy thus giving higher atom economies (Anastas et al., 2001).

Heterogenous Catalysis

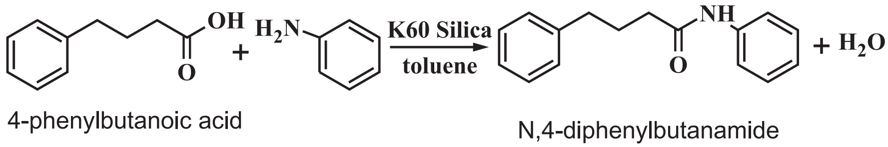
Atom economy of some reactions can be increased by using a suitable heterogenous catalyst. Here the reactant in one phase and the catalyst in a different phase interact through adsorption. As an illustration, consider the case of nickel-catalyzed hydrogenation ofnitrobenzene. The atom economy of aniline production is found to be 35% without nickel catalyst and hikes to 70% with this robust, cost-effective, easily recyclable heterogeneous catalyst, Scheme 2.28 (Grant et al., 2005).



Scheme 2.28 Nickel catalyzed hydrogenation process.

$$\% \text{ Atom economy} = \frac{93.13}{129.17} \times 100 = 72\%$$

In the case of amide bond formation, there are many inefficient coupling reagents such as phosphonium/uranium salts and carbodiimides, which not only reduce the atom economy but also forms toxic or corrosive side products (Valeur and Bradley, 2008; Constable et al., 2007). Many methods have been proposed to overcome this problem. Among them, the most significant approach is the use of readily available and affordable, thermally activated K60 Silica as a heterogenous catalyst (Comeford et al., 2009) (Scheme 2.29).

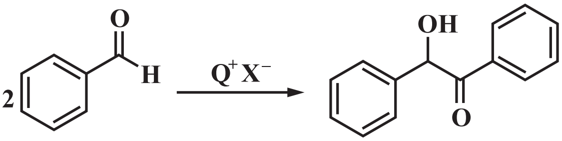


Scheme 2.29 Synthesis of N, 4-diphenylacetamide from 4-phenyl butanoic acid in presence of K60 silica catalyst.

$$\% \text{ Atom economy} = \frac{239.32}{257.33} \times 100 = 93\%$$

The above reaction of 4-phenylbutanoic acid with aniline have 74% yield with 93% atom economy although they were carried out at high temperature to inhibit the trapping of product into the silica pores. In addition, catalytic recyclability and completion of reaction were established through continuous flow experiments for industrial applications.

An important form of heterogenous catalysis is phase transfer catalysis. The transfer of a reactant from one phase into another where reaction occurs is facilitated by using phase transfer catalysts. Studies reveal that benzoin condensation in aqueous media using quaternary ammonium salt (Q^+X^-) as pseudo phase transfer catalysts (Scheme 2.30) tend to be 100% atom economical (Yadav and Kadam, 2012).



Scheme 2.30 Quaternary ammonium salt catalyzed Benzoin condensation.

$$\% \text{ Atom economy} = \frac{212.225}{212.24} \times 100 = 100\%$$

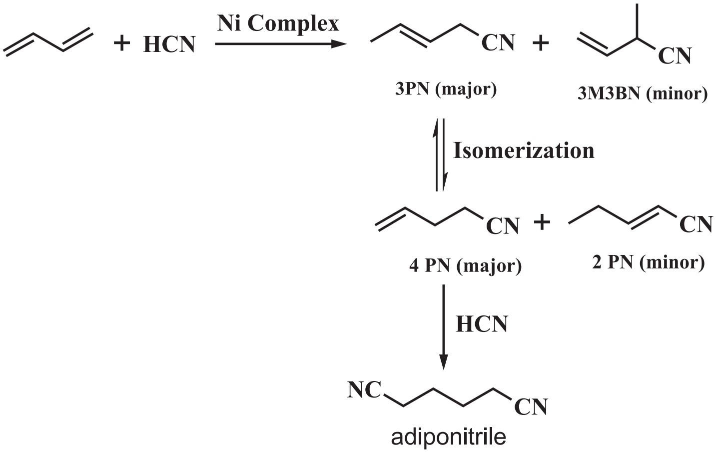
Homogenous Catalysis

Homogenous catalysis is gaining attention despite the fact that 90% of industrial processing involves heterogeneous catalysis. An important completely atom economic industrial process is the synthesis of adiponitrile using nickel-tetrakis (phosphite) complex as catalyst, given in Scheme 2.31.

$$\% \text{ Atom economy} = \frac{108.14}{108.15} \times 100 = 100\%$$

Research has progressed to improve the efficiency of catalytic reactions. Allen and Crabtree proposed such systems in the reference (Allen and Crabtree, 2010). The enhancement of atom economy in *β*-alkylation of alcohols is usually a three step process (Scheme 2.32) with minimum atom economy which can be improved by the use of an alkali metal based catalyst, which is shown in Scheme 2.33.

The suggested mechanism begins with oxidation followed by aldol condensation involving base catalyst and subsequent reduction using aluminium alkoxide catalysts. This method presents an energy efficient and cheaper process using less toxic metals, apart from the atom efficiency consideration.



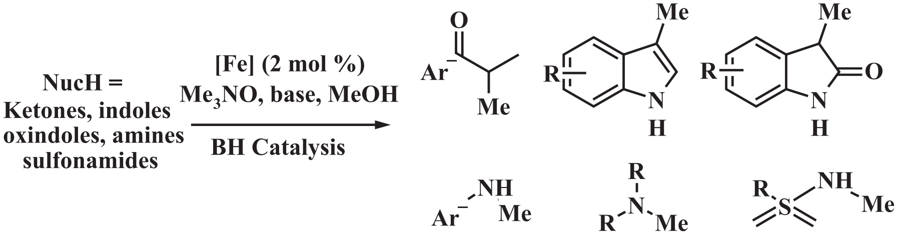
Scheme 2.31 Ni catalyzed synthesis of adiponitrile.

Scheme 2.32 Three-step beta alkylation of alcohols.

Scheme 2.33 Base catalyzed beta alkylation of secondary alcohols.

$$\%\ \text{Atom economy} = \frac{212.29}{286.42} \times 100 = 74\%$$

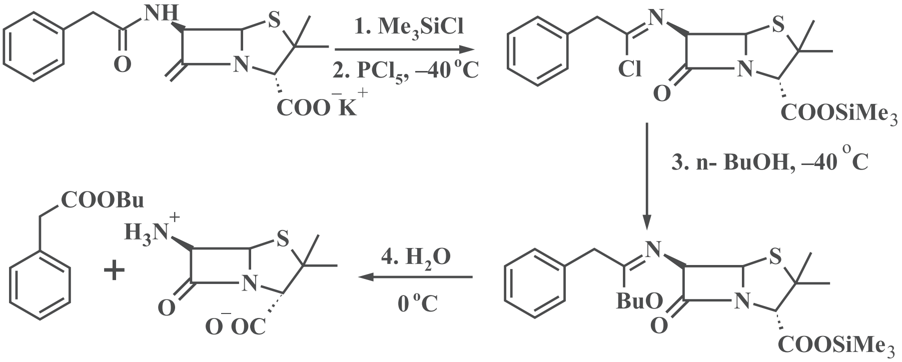
Hydrogen borrowing is another significant approach in homogenous catalysis (Berliner et al., 2011). This process combines one-pot oxidation-reaction-reduction sequence using alcohols or amines as alkylating agents with inherently high atom economy. Conventionally second and third row transition metals particularly Ru, Os, Rh and Ir were used. In need of sustainable methodologies, finding efficient alternatives becomes a major challenge. In recent times first row transition metals, which are very abundant on earth, have been established for hydrogen borrowing catalysis. Iron catalyzed methylation is the best example for the hydrogen borrowing approach using a Knölker-type (cyclopentadienone) iron carbonyl complex as a catalyst, illustrated in Scheme 2.34. A variety of amines, indoles, ketones, sulfonamides and oxindoles undergo mono- or dimethylation in excellent yields following this method (Polidano et al., 2018).



Scheme 2.34 Iron catalyzed methylation.

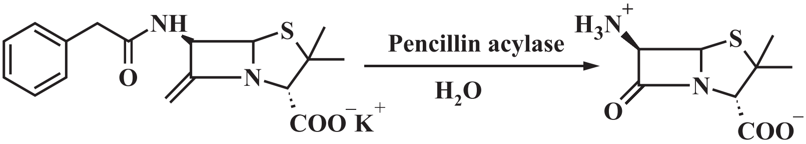
Biocatalysis

In biocatalytic processes natural catalysts such as enzymes accomplish desired transformations (Straathof et al., 2002). Modern technologies including recombinant DNA technology, immobilization methods and protein engineering providenumerous ways for realizing these reactions (Parmar et al., 2000; Powell et al., 2001). Extremely high reaction rates, high selectivity and biodegradability make enzymes a good candidate for such reactions. However high substrate specificity causes difficulties when wide substrate applicability is needed. Concerning atom economy, synthesis of 6- aminopencillanic acid from pencilin G can be considered (Scheme 2.35). Usually 6-aminopencillanic acid is synthesized through a four step deacylation process (Weissenburger and van der Hoeven, 2010).



Scheme 2.35 Synthesis of 6- aminopencillanic acid.

The mechanism includes protecting carboxyl group of penicillin G by silyl, conversion of amide into imine chloride and enol ether formation followed by hydrolysis. The atom economy of the reaction is only 28%. Later Wegman et al., 2001 demonstrated 58% atom economy by employing stable enzyme penicillin G acylase (Wegman et al., 2001), given as Scheme 2.36. Similar studies have been done extensively by completely replacing the conventional deacylation process.

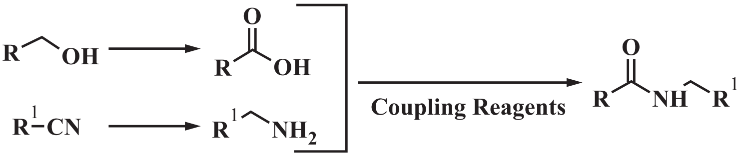


Scheme 2.36 Penicillineacylase catalyzed production of 6-amino penicillanic acid.

Research is progressing by taking atom economy as a valuable tool to design the sustainable process of pharmaceutical chemicals. Recently, Oeggl and co-workers used biocatalysts in cascades producing pharmaceutical chemicals with enhanced productivity and selectivity (Oeggl et al., 2018). In this work, all four isomers of anti-inflammatory drug 4-methoxyphenyl-12-propanediol were synthesized via two step cascade reactions using NADPH-dependent alcohol dehydrogenases. The reaction takes place with 99.9% atom economy.

Novel Examples for Catalytic Synthesis Involving 100% Atom Economy

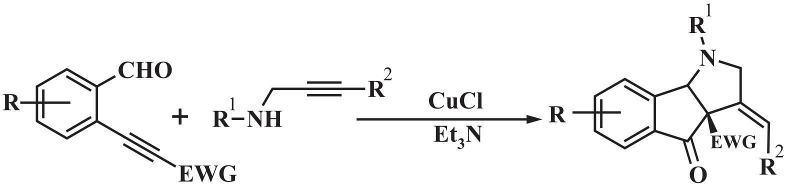
Kang and co-workers, in 2013 reported a 100% atom economical catalytic redox-neutral method for synthesis of amides from an alcohol and a nitrile (Kang et al., 2013). The earlier method of amide production is given in Scheme 2.37, which are not atom economical. Many approaches, including direct oxidation of primary alcohols and amines have been attempted for a 100 % atom economical amide synthesis (Zweifel et al., 2009; Gunanathan et al., 2007,). Ru catalyzed hydrogenation of nitriles yielding primary amines without side products had been reported (Enthaler et al., 2008; Takemoto et al., 2002). Kang et al., 2013 inspired by this, used a Ru catalyst, $RuH_2(CO)(PPh_3)_3$ for transfer of hydrogen from alcohol to nitrile, which was followed by C−N bond formation between α-carbon of the primary alcohol and nitrogen of the nitrile and yielded amides without any byproduct. The completely atom-economical redox neutral amide synthesis method is given in Scheme 2.38.



Scheme 2.37 Earlier method of amide production.

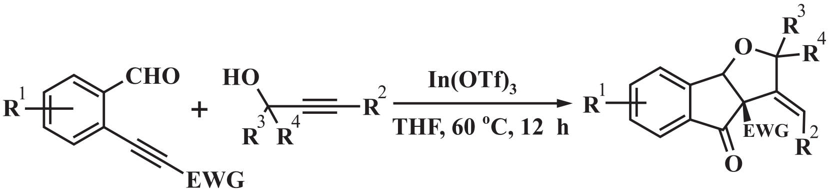
Scheme 2.38 Amide formation from alcohols and cyanides in presence of Ru catalyst.

Nitrogen-containing polycyclic compounds are essential for the agrochemical, pharmaceutical and fine chemical industries. Thus the improvement of existing methods and development of new methodologies for synthesizing nitrogen-containing polycyclic compounds are very important. Qiu et al. in 2017 reported a 100% atom economic method for synthesizing indanone fused pyrrolidine from enynals and propargylamines using CuCl/Et_3N as the catalyst, which is given in Scheme 2.39. Here in this reaction, two rings and four bonds are formed in a single step with high atom economy.



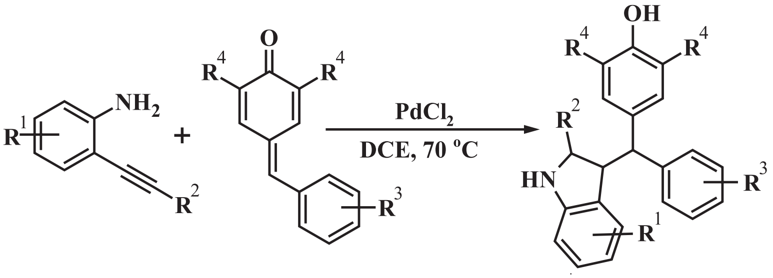
Scheme 2.39 Indanone fused pyrrolidine synthesis in presence of CuCl/Et_3N catalyst.

Large varieties of natural bioactive compounds, such as lignans, terpenes, steroids, nucleosides, etc. contain 2-methylene tetrahydrofurans and g-lactones as their core structures. Also the polycyclic structures such as euchroquinol, tricholomalide, parthenolide, dehydrocostus lactone, solanacol, etc. are formed by fusing these skeletons with other cyclic units. But all these syntheses require multisteps with low atom and step economy. Thus development of an efficient method for the synthesis of polycyclic compounds containing 2-methylene tetrahydrofuran and g-lactone units is of great importance. Liang in 2016 reported a 100% atom economic one pot rapid process for synthesizing indanone-fused 2-methylene tetrahydrofurans from enynals and propynols, which involves hydrolysis, followed by Knoevenagel condensation, Michael addition and Conia-ene reactions (Liang et al., 2016), which is illustrated in Scheme 2.40. Here in this method two rings and four bonds are formed with complete atom-economy.



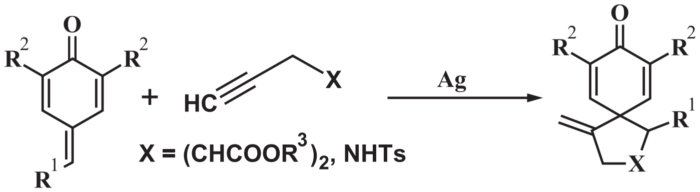
Scheme 2.40 Synthesis of indanone-fused tetrahydrofurans in presence of Indium catalyst.

Tri aryl methanes find various applications in medicinal chemistry and the dye industry. They also find various applications in material science, mostly as photochromic agents and fluorescent probes. Reddy and Vijaya in 2015 reported a highly efficient, 100% atom economic, one pot methodology (Scheme 2.41) for the synthesis of unsymmetrical diarylindolyl methane derivatives by a Pd catalyzed addition of o-alkynyl anilines to p-quinonemethides (Reddy and Vijaya, 2015). The main features of this methodology are its 100% atom economy and its broad substrate scope. Unlike the reported methodologies so far, this method does not need the protection of the amino group.



Scheme 2.41 Pd catalyzed synthesis of unsymmetrical diarylindolyl methane derivatives.

Many natural products and bioactive molecules contain spiro[4,5]cyclohexadienones as their skeletons. Hence they are considered as dominant intermediates in many natural product syntheses. Traditional methods for the synthesis of spiro[4,5]cyclohexadienones are intra molecular dearomatization reaction of phenol derivatives. These reactions need the use of heavy metals and hard reaction conditions. Yuan in 2017 reported a highly efficient, 100% atom economic method for the synthesis of spiro[4,5]cyclohexadienones from para-quinonemethides and propargylmalonates through a silver-catalyzed 1,6-addition reaction (Yuan et al., 2017), explained in Scheme 2.42.



Scheme 2.42 Silver catalyzed synthesis of spiro[4,5]cyclohexadienones.

CHEMISTRY OF NANOSIZED METAL PARTICLES VIA ATOM ECONOMY CONCEPT

In the modern era, advanced technologies for synthesis are gaining wide attention. In case of metal nanoparticle synthesis, a long standing dilemma exists between the classical top-down and bottom-up approach. Although each method is significant in some way, size control is a crucial problem with physical methods. Even though the colloidal approach can address the problem, low yields hamper the advantage. Moreover, large scale production of monodisperse nanoparticles cannot be achieved using physical methods. An atom economical approach could be more feasible in this context. Selecting reagents with multiple capability and reducing reagents eliminates unwanted products and purification processes. Wostek et al. investigated nanoparticles of Ru, Co and Rh through decomposition of organo metallic precursors (Wostek et al., 2005). Greckler and co-workers synthesized Au nanoparticle using poly(vinylpyrrolidone) as the protecting agent and NaBH$_4$ as the reducing agent in the solid state using high speed vibration milling (Debnath et al., 2009).

In 2010, Kalidindi and co-workers suggested a facile green route (scheme) for synthesizing air stable Cu, Ag and Au nanoparticles. The method used the mechanical stirring of mixtures of a metal salt and ammonia borane. Ammonia borane plays both the role of a reducing agent and the precursor for the stabilizing agent. Here ammonia borane is maintained at 60°C in an oil bath and metal salt is added in small batches under an inert atmosphere. The resulting powders are desired metal nanoparticles of corresponding metal salts.

The metal particles formed can be identified from the color of the final product. For example, $CuCl_2$ has a brown color, while the copper nanoparticle has a reddish brown appearance.

OTHER CONCEPTS RELATED TO ATOM ECONOMY

There are various other measures, which can be used for calculating the greenness of a chemical reaction. Selectivity, E-factor, effective mass yield, reaction mass efficiency, etc. are some concepts related to atom economy utilised in green chemistry (Sheldon, 2018; Andaros and Sayed, 2007; Hudson et al., 2016). Selectivity is a widely accepted concept for measuring the greenness of a reaction and is described in detail below.

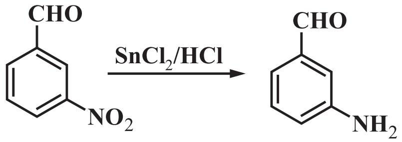
Selectivity

Selectivity is one of the important concepts in green chemistry and arises when we have to control the reaction to get the desired product over side products. Selectivity is related to yield an atom economy. A number of compounds are prepared through selective reactions. Selectivity is influenced by steric and electronic effects. Depending on the nature of selection chemoselectivity (functional group reactivity), regioselectivity (orientation) and stereoselectivity (spatial arrangement) can be defined (Trost, 1983).

Chemoselectivity

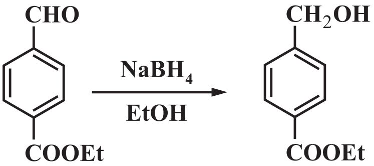
According to IUPAC, Chemoselectivity is defined as “the preferential reaction of a chemical reagent with one of two or more different functional groups” (Shenvi et al., 2009). In the absence of chemoselective reagents the reaction is indiscriminate and all possible products are formed, decreasing the atom economy of the process. Chemoselectivity becomes important when complex organic molecules with more than one reactive site or functional groups are involved in the reaction. In this case, the reagent has to be directed to the preferred site for the desired outcome. The discrimination ability of a reagent, the ability of the reagent to select sites to react with it, is called chemoselectivity (Trost, 1983).

For example, $SnCl_2/HCl$ does not react with –CHO group, when both the nitro and aldehyde groups are present in the same molecule. Thus only the nitro group will be reduced as shown in the Scheme 2.43.



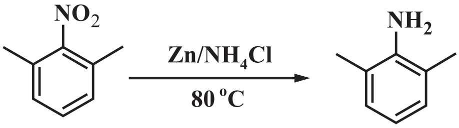
Scheme 2.43 Reduction using $SnCl_2/HCl$.

Another example is the reduction of –CHO group to $–CH_2OH$ in presence of another substituent –COOEt group, by $NaBH_4$ as reducing agent, given in Scheme 2.44.



Scheme 2.44 Reduction using $NaBH_4$.

Most of the industrial synthesis of dyes, medicinal supplies, agricultural chemicals, etc. is accompanied by reduction of nitroarenes to aromatic amines (Tsukinoki and Tsuzuki, 2001). The conventional procedure for reduction of aromatic nitro compounds requires organic solvents under drastic conditions and irritant reagents like NH_3, conc.HCl or 20% aq. NaOH, so this reaction is not environmentally benign. To make the reaction green Zinc metal and NH_4Cl in water at 80°C can be used as reducing agents. The sterically hindered 2,6-dimethylnitrobenzene can be reduced selectively by these reagents, which is shown in Scheme 2.45. The reaction is chemoselective for nitrogroups only; other substituents such as amide, ester and halide on aromatic rings are rarely affected.



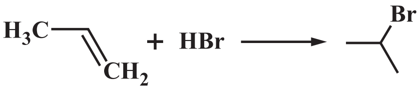
Scheme 2.45 Reduction using Zn/NH_4Cl.

Regioselectivity

In regioselective reactions, one of the positional isomer is preferentially formed. The question of regioselectivity arises when a reagent can approach a particular reactive site through different regions or positions. A regioselective reagent is required to obtain the desired product. A simple example is addition of HX over an unsymmetrical olefin.

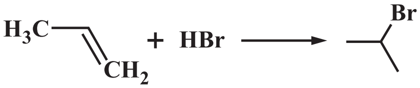
Example: Reaction of Propene with HBr

(a) In the absence of hydrogenperoxide - Markovnikov's addition: The positive end goes to the carbon having more number of hydrogen atoms (Scheme 2.46).



Scheme 2.46 Markovnikov's addition.

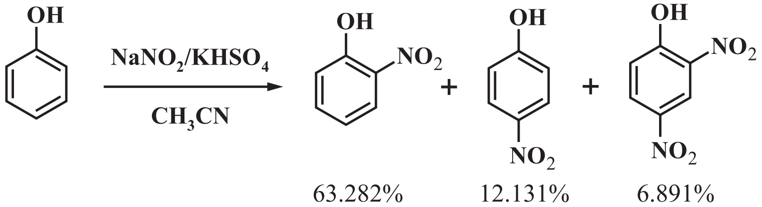
(b) In the presence of hydrogenperoxide—AntiMarkovnikov's addition: The positive end goes to carbon having lesser number of hydrogen atoms (Scheme 2.47).



Scheme 2.47 AntiMarkovnikov's addition.

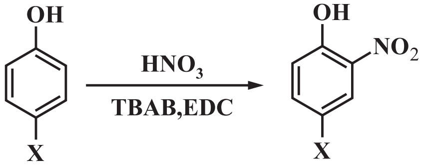
Traditional procedure for the nitration of phenol is the use of conc. nitric acid and sulfuric acid. The products obtained here are ortho- nitrophenol, para-nitrophenol and dinitro phenol. i.e. the nitration of phenol is not selective.

Regio selective ortho nitration of phenol can be done by using $NaNO_2/KHSO_4$ in CH_3CN (Heravi et al., 2007), Scheme 2.48. The reagent used is also inexpensive, easy to handle and ecofriendly compared to the traditional nitration reagents.



Scheme 2.48 Regio selective orthonitration of phenol.

Another regioselective method for the nitration of phenol and substituted phenols is the use of dilute HNO_3 in the presence of a phase transfer catalyst tetrabutylammonium bromide (TBAB) using ethylene dichloride (EDC) as a solvent (Joshi et al., 2003), given in Scheme 2.49. As a consequence, reaction rate increases, yield increases and production of waste reduce. The nitration data of phenol and substituted phenols using different mol% of phase transfer catalyst reagent is provided in Table 2.1.



where X = CH_3, Cl or F

Scheme 2.49 Nitration using HNO_3 in presence of TBAB.

Table 2.1 Nitration with phenol and substituted phenols (Joshi et al., 2003)

Sl no.	*Reactant*	*TBAB* (mol%)	*Time* (hours)	*% Yield*
1	Phenol	0	4	0.4
2	Phenol	5	4	90
3	4-Cresol	10	5	97
4	4-Chlorophenol	10	6	97
5	4-Fluorophenol	10	6	97

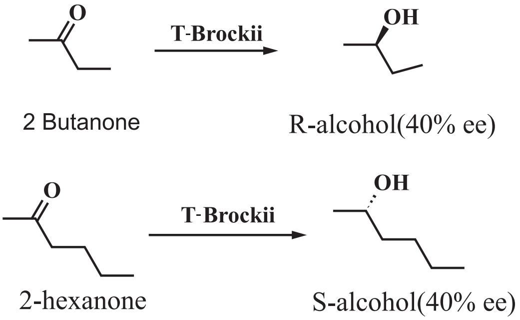
Stereoselectivity

Stereoselectivity in a reaction allows preferential formation of one stereoisomer in the reaction. Stereoisomers differ only in the spatial orientation of constituent atoms in space. Stereoisomers can be optically active or inactive. Stereoisomers that are mirror images are called enantiomers and those that are not mirror images are called diastereomers. Stereoselectivity have been achieved in many cases between enantiomers and diastereomers. They are considered separately below.

a) Enantioselectivity

In enentioselective reactions, one enantiomer is formed preferentially over the other. Enantiomers have similar physical and chemical properties, but significantly differ in biological activity. Enantiomers are optically active and contain chiral reaction centers. Hence chiral features in substrate, reagent or catalyst are required for an enantioselective reaction to occur. Non-chiral reagents produce racemic mixtures as products. Enantioselectivity is of great importance in pharmaceutical chemistry (Federsel, 2005) and agrochemistry, particularly in cases where one enantiomer has good efficiency and is non toxicity, while the other one has no activity and is toxic. Consider the case of ibuprofen, a pain killer. The S-form of the molecule is an effective analgesic while the R-form is inactive. As separation of two forms is difficult, the drug is supplied as a racemic mixture. Enantioselective synthesis of ibuprofen has been addressed in may research reports (Acemoglu and Williams, 2003; Tanaka et al., 2001).

An example of enantioselective reaction is the reduction of ketone using the enzyme Thermoanaerobiumbrockii. Lower ketones like 2-butanone produce R-alcohol and higher ketones like 2-hexanone produce S-alcohol (Scheme 2.50).

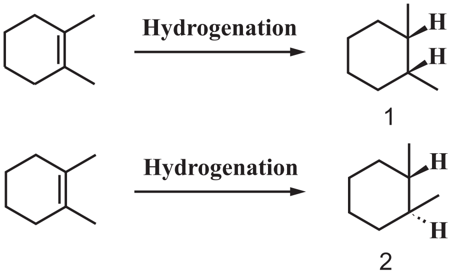


Scheme 2.50 Enantio selective reduction of ketone with Thermoanaerobiumbrockii.

'ee' is the enantiomeric excess, which is the differencein mole fractions of enantiomers in the mixture, used to measure degree of selectivity. Since a racemic mixture contains equal amount of enantiomers, the enantiomeric excess is zero. If a mixture contains the (+) enantiomer in four times than (–) enantiomer, the difference is 0.8–0.2 = 0.6 or 60% ee. A pure enantiomer has 100% ee.

b) Diastereoselectivity

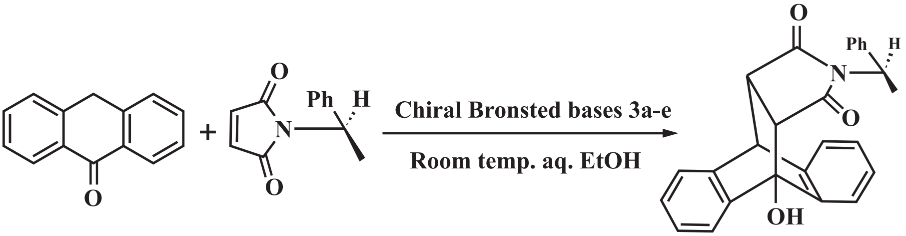
Consider the hydrogenation of substituted cyclohexene given in Scheme 2.51.



Scheme 2.51 Hydrogenation of substituted cyclohexene.

Addition of the two hydrogen atoms through the same side of the plane of the double bond, results in product I and through opposite sides results in product II. Catalytic hydrogenation usually results in product I rather than II since the hydrogen atoms are delivered from the catalyst surface, on one side. The two products are diastereomers.

This preferential formation of one diastereomer over the other is called diastereoselectivity. Diastereomers contain more than one chiral center. Consider the reaction between anthrone and R(+)-N-α-methyl benzyl maleimide in the presence of triethyl amine as achiral base in water-ethanol medium, given in Scheme 2.52. The reaction has excellent yields, but is not diastereoselective. Instead of the achiral base, chiral Brownsted bases like cinchonine, quinine, etc. produce diastereoselective products.



Scheme 2.52 Reaction between anthrone and R-(+)-N-α-methyl benzyl maleimide in the presence of triethyl amine.

E-Factor

Waste production is an unavoidable consequence of industrial production. Managing the waste problem is of prime importance in green and sustainable chemistry. One aspect of minimizing waste production is recycling reagents and solvents. If catalysts and reagents are in the solid phase, they can be filtered off and reused. Substrate materials are continuously added to yield the product which is simultaneously removed, while heterogeneous reagents and catalysts are kept stationary. Environmental factor (E-factor) was introduced by Roger Sheldon to determine the mass efficiency of such type of chemical reactions (Andaros, 2009). E-factor can be effectively used as a tool to measure how much waste is generated. It gives a perspective on the environmental impact of a particular reaction.

$$\textit{E-factor} = \frac{\text{Mass of produced wastes}}{\text{Mass of desired product}}$$

Since estimation of the exact amount of wastes is difficult, an easier way of calculating the E-factor is given below.

$$\textit{E-factor} = \frac{\text{Mass of raw materials} - \text{Mass of product}}{\text{Mass of product}}$$

For almost all petroleum refining processes E-factors have been estimated to be close to zero, an ideal production with zero waste generation. But in the case of pharmaceutical and fine chemical industries, E-factors have been estimated to be very high, in the range 5–100, indicating production of a large amount of waste. The E-factors of various industries is given in Table 2.2.

E-factor and other concepts do not discuss the toxicity of wastes. For comparison of alternate processes, we need to consider the toxicity aspect , along with the amount of waste production. The term Environmental Quotient (EQ) was proposed and is calculated as the product of E-factor and a correction factor Q (unfriendliness quotient). The unfriendliness quotient, Q is the measure of toxic substances. If Q-factor is 1, the waste has no environmental impact. The waste can be recycled, if the E-factor is less than 1 and the wastes produced are toxic, hazardous and cannot be recycled, if it is greater than 1.

Table 2.2 E-factors for different sectors of chemical industry (Sheldon, 2008)

Industry sector	***Annual production*** **(tones)**	***E-factor***
Oil refining	10^6–10^8	Less than 0.1
Bulk chemicals	10^4–10^6	≤ 1
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–100

We can compare E-factor of various chemical industries. Production of bulk chemicals is highly efficient compared to the production of fine chemicals and pharmaceuticals. Use of inorganic reagents such as metals (Zn, Fe), metal hydrides ($NaBH_4$, $LiAlH_4$), etc. in reduction steps and $KMnO_4$, $K_2Cr_2O_7$ etc. in oxidation steps helps in decreasing the E-factor. Many reactions are accelerated by Lewis acids ($AlCl_3$, BF_3, $ZnCl_2$) or mineral acids (H_2SO_4, H_3PO_4, HF). Substituting outdated stoichiometric approaches with suitable catalytic alternatives is a way to manage the waste. A catalytic process in which hydrogen acts as a reducing agent is more atom efficient than a hydride reducing agent. Similarly in comparison of E-factors of different oxidants, oxygen has less E-factor than other oxidants and is more reliable.

Effective mass yield (EMY)

Another concept related to atom economy is the Effective Mass Yield (EMY) proposed by Hudlicky

$$\text{EMY} = \frac{\text{Mass of desired product}}{\text{Mass of non-benign reagents}} \times 100$$

A non benign substance is defined as those by-products, solvents or surplus reagents being associated with environmental threats. The difficulty to find out whether the reagent is non benign or not is the major drawback of this concept. The scarcity of toxicology data and measuring of non-benign nature makes this parameter a less useful one.

Reaction Mass Efficiency (RME)

We cannot ensure that a reaction with high atom economy will give high yields or vice versa. So a need for a better quantitative measure arises, which accounts for both yield and atom economy. Reaction Mass Efficiency (RME), also called real atom economy is a more realistic metric for describing the greenness of a chemical reaction, put forward by Constable et al. at Glaxo Smith Kline in 2002. RME comprises yield, stoichiometry and atom economy and thus can be considered as a superior tool among all.

$$\text{RME} = \frac{\text{Mass of desired product}}{\text{Total mass of reactants}} \times 100\%$$

It can be expressed in another way as,

$$\text{RME} = \text{Yield} \times \text{Atom economy} \times \frac{1}{\text{Stoichiometric factor}}$$

Consider the esterification reaction of n- butanol with acetic acid to form n-butyl acetate ester, as an example for illustration (Table 2.3).

Table 2.3 Number of moles calculation for esterification reaction of n- butanol with acetic acid

Reactant/Product	*Mol. weight* (g)	*Mass* (g)	*No. of moles*
n-Butanol	74	37	0.5
Acetic acid	60	60	1
Acetate ester	116	40	0.34

$$\text{Yield} = \frac{0.34}{0.5} \times 100 = 68\%$$

$$\text{Atom economy} = \frac{116}{74 + 60} \times 100 = 87\%$$

From the calculation, it is clear that, this esterification reaction is green in atom economical context, but in terms of yield, it is only moderately green. Here we can calculate the RME, which is a measure encompassing both these aspects.

$$\text{RME} = \frac{40}{97} \times 100 = 41\%$$

As one can imagine multiple factors need to be taken into account to access the greenness of a process along with atom economy. Recently multi-metric analysis including acidification potential, smog formation potential, global warming potential, ozone depletion potential, abiotic resource depletion potential, persistence, bioaccumulation, ingestion toxicity, inhalation toxicity, etc. of different synthetic routes of aniline from benzene have been attempted to identify the greener process (Mercer et al., 2012). Similar assessments are required to completely characterize a process as being completely green.

CONCLUSION

Use of green chemistry and green principles are going to be pivotal if sustainable life is to be established on earth. It is high time that our synthetic methodologies and industrial production are revamped to align with green principles that outline safe, sustainable and waste minimizing synthetic methods. Among the 12 principles of green chemistry, the second one, concept of atom economy allows a quantitative estimation of greenness of a synthetic process. The process with higher atom economy is expected to result in low wastage. But one needs to keep in mind that it does not encapsulate product yield, extend of waste generation or nature of waste. Definitions with wider scope that can reflect toxicity, nature and management of waste, general usefulness and environmental impact would be required to precisely quantify the environmental and sustainability impact of a chemical process.

REFERENCES

Acemoglu, L., Williams, J.M.J. Palladium-catalysed enantioselective synthesis of ibuprofen. *Journal of Molecular Catalysis A: Chemical,* 2003, 196(1–2), 3–11.

Allen, L.J., Crabtree, R.H. Green alcohol couplings without transition metal catalysts: base-mediated β-alkylation of alcohols in aerobic conditions. *Green Chemistry,* 2010, 12(8), 1362–1364.

Anastas, P.T., Kirchhoff, M.M., Williamson, T.C. Catalysis as a foundational pillar of green chemistry. *Applied Catalysis A: General,* 2001, 221(1–2), 3–13.

Anastas, P.T., Kirchhoff, M.M. Origins, current status, and future challenges of green chemistry. *Journal of Chemical Education,* 2002, 35(9), 686–694.

Andraos, J. Unification of reaction metrics for green chemistry: Applications to reaction analysis. *Organic Process Research and Development,* 2005a, 9(2), 149–163.

Andraos, J. Unification of reaction metrics for green chemistry ii: Evaluation of named organic reactions and application to reaction discovery. *Organic Process Research and Development,* 2005b, 9(4), 404–431.

Andraos, J., Sayed, M. On the use of “Green” metrics in the undergraduate organic chemistry lecture and lab to assess the mass efficiency of organic reactions. *Journal of Chemical Education,* 2007, 84(6), 1004.

Andraos, J. Global green chemistry metrics analysis algorithm and spreadsheets: Evaluation of the material efficiency performances of synthesis plans for oseltamivir phosphate (Tamiflu) as a test case. *Organic Process Research and Development,* 2009, 13(2), 161–185.

Barrett, A.G.M., Braddock, D.C., James, R.A., Koike, N., Procopiou, P.A. Nucleophilic substitution reactions of (Alkoxymethylene) dimethylammonium chloride. *Journal of Organic Chemistry,* 1998, 63(18), 6273–6280.

Berliner, M.A., Dubant, S.P.A., Makowski, T., Ng, K., Sitter, B., Wager, C., Zhang, Y. Use of an iridium-catalyzed redox-neutral alcohol-amine coupling on kilogram scale for the synthesis of a GlyT1 inhibitor. *Organic Process Research and Development,* 2011, 15(5), 1052–1062.

Cann, M.C., Dickneider, T.A. Infusing the chemistry curriculum with green chemistry using real-world examples, web modules, and atom economy in organic chemistry courses. *Journal of Chemical Education,* 2004, 81(7), 977–980.

Choudary, B.M., Chowdari, N.S., Madhi, S., Kantam, M.L. A trifunctional catalyst for one-pot synthesis of chiral diols via heck Coupling−N-Oxidation−Asymmetric dihydroxylation: Application for the synthesis of diltiazem and taxol side chain. *Journal of Organic Chemistry,* 2003, 68(5), 1736–1746.

Comerford, J.W., Clark, J.H., Macquarrie, D.J., Breeden, S.W. Clean, reusable and low cost heterogeneous catalyst for amide synthesis. *Chemical Communications,* 2009, 18, 2562–2564.

Constable, D.J.C., Curzons, A.D., Cunningham, V.L. Metrics to ‘Green’ chemistry—which are the best? *Green Chemistry,* 2002, 4(6), 521–527.

Constable, D.J.C., Dunn, P.J., Hayler, J.D., Humphrey, G.R., Leazer, J.L. Jr., Linderman, R.J., Lorenz, K., Manley, J., Pearlman, B.A., Wells, A., Zaks, A., Zhang, T.Y. Key green chemistry research areas—A perspective from pharmaceutical manufacturers. *Green Chemistry,* 2007, 9(5), 411–420.

Debnath, D., Kim, S.H., Geckeler, K.E. The first solid-phase route to fabricate and size-tune gold nanoparticles at room temperature. *Journal of Material Chemistry,* 2009, 19(46), 8810.

Dömling, A. Recent advances in isocyanide-based multicomponent chemistry. *Current Opinion in Chemical Biology,* 2002, 6(3), 306–313.

Eissen, M., Mazur, R., Quebbemann, H.G., Pennemann, K.H. Atom economy and yield of synthesis sequences. *Helvetica Chimica Acta*, 2004, 87(2), 524–535.

Enthaler, S., Junge, K., Addis, D., Erre, G., Beller, M. A practical and benign synthesis of primary amines through ruthenium-catalyzed reduction of nitriles. *ChemSusChem,* 2008, 1(12), 1006–1010.

Federsel, H.J. Asymmetry on large scale: the roadmap to stereoselective processes. *Nature Reviews Drug Discovery*, 2005, 4, 685.

Fennie, M.W., Roth, J.M. Comparing amide-forming reactions using green chemistry metrics in an undergraduate organic laboratory. *Journal of Chemical Education,* 2016, 93(10), 1788–1793.

Fishback, V., Reid, B., Schildkret, A. Three modules incorporating cost analysis, green principles, and metrics for a sophomore organic chemistry laboratory. *ACS Symposium Series,* 2016, 1233, 33–53.

Geier, S.J., Chase, P.A., Stephan, D.W. Metal-free reductions of n-heterocycles via lewis acid catalyzed hydrogenation. *Chemical Communications,* 2010, 46(27), 4884–4886.

Grant, S., Freer, A.A., Winfield, J.M., Gray, C., Lennon, D. Introducing undergraduates to green chemistry: An interactive teaching exercise. *Green Chemistry,* 2005, 7(3), 121–128.

Gunanathan, C., Ben-David, Y., Milstein, D. Direct synthesis of amides from alcohols and amines with liberation of H_2. *Science,* 2007, 317(5839), 790–792.

Heravi, M.M., Oskooie, H.A., Baghernejad, B. Facile, Regioselective and green synthesis of ortho-nitrophenoles using $NaNO_2$, $KHSO_4$. *Journal of the Chinese Chemical Society,* 2007, 54(3), 767–770.

Hudson, R., Leaman, D., Kawamura, K.E., Esdale, K.N., Glaisher, S., Bishop, A., Katz, J.L. Exploring green chemistry metrics with interlocking building block molecular models. *Journal of Chemical Education,* 2016, 93(4), 691–694.

Joshi, A.V., Baidoosi, M., Mukhopadhyay, S., Sasson, Y. Nitration of phenol and substituted phenols with dilute nitric acid using phase-transfer catalysts. *Organic Process Research and Development,* 2003, 7(1), 95–97.

Kalidindi, S.B., Sanyal, U., Jagirdar, B.R. Metal nanoparticles via the atom-economy green approach. *Inorganic Chemistry,* 2010, 49(9), 3965–3967.

Kang, B., Fu, Z., Hong, S.H. Ruthenium-catalyzed redox-neutral and single-step amide synthesis from alcohol and nitrile with complete atom economy. *Journal of American Chemical Society,* 2013, 135(32), 11704–11707.

Kidwai, M., Mohan, R. Green chemistry: An innovative technology. *Foundations of Chemistry,* 2005, 7(3), 269–287.

Li, C.J., Trost, B.M. Green chemistry for chemical synthesis. *Proceedings of the National Academy of Sciences,* 2008, 105(36), 13197–13202.

Liang, R., Chen, K., Zhang, Q., Zhang, J., Jiang, H., Zhu, S. Rapid access to 2-methylene tetrahydrofurans and γ-lactones: A tandem four-step process. *Angewandte Chemie International Edition,* 2016, 55(7), 2587–2591.

McKenzie, L.C., Huffman, L.M., Hutchison, J.E. The evolution of a green chemistry laboratory experiment: greener brominations of stilbene. *Journal of Chemical Education,* 2005, 82(2), 306–310.

Mercer, S.M., Andraos, J., Jessop, P.G. Choosing the greenest synthesis: a multivariate metric green chemistry exercise. *Journal of Chemical Education,* 2012, 89(2), 215–220.

Nguyen, T.B., Retailleau, P. Redox-neutral access to sultams from 2-Nitrochalcones and sulfur with complete atom economy. *Organic Letters,* 2017, 19(14), 3879–3882.

Oeggl, R., Maßmann, T., Jupke, A., Rother, D. Four atom efficient enzyme cascades for all 4-Methoxyphenyl-1,2-Propanediol isomers including product crystallization targeting high product concentrations and excellent E-factors. *ACS Sustainable Chemistry and Engineering,* 2018, 6(9), 11819–11826.

Parmar, A., Kumar, H., Marwaha, S., Kennedy, J. Advances in enzymatic transformation of penicillins to 6-Aminopenicillanic acid (6-APA). *Biotechnology Advances,* 2000, 18(4), 289–301.

Polidano, K., Allen, B.D.W., Williams, J.M.J., Morrill, L.C. Iron-catalyzed methylation using the borrowing hydrogen approach. *ACS Catalysis,* 2018, 8(7), 6440–6445.

Posner, G.H. Multicomponent one-pot annulations forming 3 to 6 bonds. *Chemical Reviews,* 1986, 86(5), 831–844.

Powell, K.A., Ramer, S.W., del Cardayré, S.B., Stemmer, W.P.C., Tobin, M.B., Longchamp, P.F., Huisman, G.W. Directed evolution and biocatalysis. *Angewandte Chemie International Edition,* 2001, 40(21), 3948–3959.

Qiu, S., Chen, L., Jiang, H., Zhu, S. CuCl/Et_3 N-catalyzed synthesis of indanone-fused 2-Methylene pyrrolidines from enynals and propargylamines. *Organic Letters,* 2017, 19(17), 4540–4543.

Reddy, V., Vijaya Anand, R. Expedient access to unsymmetrical diarylindolylmethanes through palladium-catalyzed domino electrophilic cyclization–extended conjugate addition approach. *Organic Letters*, 2015, 17(14), 3390–3393.

Sato, K.A. "Green" Route to adipic acid: Direct oxidation of cyclohexenes with 30 percent hydrogen peroxide. *Science*, 1998, 281(5383), 1646–1647.

Sheldon, R.A. E factors, green chemistry and catalysis: An odyssey. *Chemical Communications,* 2008, 29, 3352–3365.

Sheldon, R.A. Metrics of green chemistry and sustainability: Past, present, and future. *ACS Sustainable Chemistry and Engineering,* 2018, 6(1), 32–48.

Shenvi, R.A., O'Malley, D.P., Baran, P.S. Chemoselectivity: The mother of invention in total synthesis. *Accounts of Chemical Research,* 2009, 42(4), 530–541.

Sipos, G., Gyollai, V., Sipőcz, T., Dormán, G., Kocsis, L., Jones, R.V., Darvas, F. Important industrial procedures revisited in flow: Very efficient oxidation and *N*-Alkylation reactions with high atom-economy. *Journal of Flow Chemistry,* 2013, 3(2), 51–58.

Song, Y., Wang, Y., Geng, Z. Some exercises reflecting green chemistry concepts. *Journal of Chemical Education,* 2004, 81(5), 691–692.

Straathof, A.J., Panke, S., Schmid, A. The production of fine chemicals by biotransformations. *Current Opinion in Biotechnology,* 2002, 13(6), 548–556.

Takemoto, S., Kawamura, H., Yamada, Y., Okada, T., Ono, A., Yoshikawa, E., Mizobe, Y., Hidai, M. Ruthenium complexes containing bis(diarylamido)/Thioether ligands: synthesis and their catalysis for the hydrogenation of benzonitrile. *Organometallics,* 2002, 21(19), 3897–3904.

Tanaka, J.I., Oda, S., Ohta, H. Synthesis of (S)-Ibuprofen via enantioselective degradation of racemic ibuprofen with an isolated yeast, trichosporon cutaneum KPY 30802, in an interface bioreactor. *Journal of Bioscience and Bioengineering*, 2001, 91(3), 314–315.

Trost, B.M. Selectivity: A key to synthetic efficiency. *Science,* 1983, 219(4582), 245–250.

Trost, B.M. Atom economy-a challenge for organic synthesis: Homogeneous catalysis leads the way. *Angewandte Chemie International Edition in English,* 1995, 34(3), 259–281.

Trost, B.M. On inventing reactions for atom economy. *Accounts of Chemical Research,* 2002, 35(9), 695–705.

Tsukinoki, T., Tsuzuki, H. Organic reaction in water. Part 5.1 novel synthesis of anilines by zinc metal-mediated chemoselective reduction of nitroarenes. *Green Chemistry*, 2001, 3(1), 37–38.

Ugi, I., Dömling, A., Hörl, W. Multicomponent reactions in organic chemistry. *Endeavour,* 1994, 18(3), 115–122.

Valeur, E., Bradley, M. Amide bond formation: Beyond the myth of coupling reagents. *Chemical Society Reviews,* 2008, 38(2), 606–631.

Wardman, P. Reduction potentials of one-electron couples involving free radicals in aqueous solution. *Journal of Physical Chemistry Reference Data,* 1989, 18(4), 1637–1755.

Wegman, M.A., Janssen, M.H.A., van Rantwijk, F., Sheldon, R.A. Towards biocatalytic synthesis of β-lactam antibiotics. *Advanced Synthesis and Catalysis,* 2001, 343(6–7), 559–576.

Weissenburger, H.W.O., van der Hoeven, M.G. An efficient nonenzymatic conversion of benzylpenicillin to 6-aminopenicillanic acid. *Recueil des Travaux Chimiquesdes Pays-Bas,* 2010, 89(10), 1081–1084.

Wostek-Wojciechowska, D., Jeszka, J.K., Amiens, C., Chaudret, B., Lecante, P. The solid-state synthesis of metal nanoparticles from organometallic precursors. *Journal of Colloid and Interface Science,* 2005, 287(1), 107–113.

Yadav, G.D., Kadam, A.A. Atom-efficient benzoin condensation in liquid–liquid system using quaternary ammonium salts: pseudo-phase transfer catalysis. *Organic Process Research and Development,* 2012, 16(5), 755–763.

Yuan, Z., Liu, L., Pan, R., Yao, H., Lin, A. Silver-catalyzed cascade 1,6-addition/cyclization of *para* -quinone methides with propargyl malonates: An approach to spiro[4.5]deca-6,9-dien-8-ones. *Journal of Organic Chemistry,* 2017, 82(16), 8743–8751.

Zweifel, T., Naubron, J.V., Grützmacher, H. Catalyzed dehydrogenative coupling of primary alcohols with water, methanol, or amines. *Angewandte Chemie,* 2009, 121(3), 567–571.

RECENT DEVELOPMENTS
IN
COMMERCE AND MANAGEMENT

EDITORS
Dr .P. VASANTHAKUMARI
Mrs. DEEPA.C
Mrs. SWAPNA.K

P.G DEPARTMENT OF COMMERCE
N.S.S COLLEGE, OTTAPALAM

English
RECENT DEVELOPMENTS IN COMMERCE AND MANAGEMENT
(Studies)

Editor : ***Dr .P. VASANTHAKUMARI***

First Published : June 2020
Cover Design : Book Media, Pala
Layout : Amrutha Syam
Printing : Book Media

Publishing
P.G Department of Commerce
N.S.S College, Ottapalam

Distribution
BOOK MEDIA
Pala - 686 575
Kottayam, Kerala, India.
Mobile +91 94475 36240
ISBN: 978-81-945634-02

Editorial

The growing Phenomenon of globalization, liberalization and Privatization has been immensely influencing the commerce and management field. Within the last decade, a lot of new trends have emerged in commerce and management field with a profound influence. The broad aim of this international conference was to explore and provide a platform of debate about global and nationwide developments in commerce and management. The seminar submissions in the form of paper on different aspects on the scheme after review process have been enclosed in this edited book.

We extend our profound thanks to the Management, The Principal, State bank of India, Regional branch, Shornur and resource persons who contributed greatly to this conference .We sincerely congratulate and thank all the authors for contributing their creative research work to this conference. We are also grateful to Book media who have helped to publish this edited Book.

Dr.P. Vasanthakumari
Head of the Department of commerce
N.S.SCollege, Ottapalam

ROLE OF PRIME MINISTER'S EMPLOYMENT GENERATION PROGRAMME TO PROMOTE ENTREPRENEURSHIP IN KERALA

Seena P P
Assistant professor
Dept. of Commerce
S.E.S College, Sreekandapuram

Dr.Swarupa R
Associate professor and research guide
Dept. of Commerce
M.G College, Iritty

Abstract

Unemployment is the crucial problem faced by the youth of the nation. Idustrialisation is the solution for economic growth and employment generation. Govt of India introduced a credit linked capital subsidy scheme named Prime Minister's Employment Generation Programme to generate employment opportunities by setiing up micro enterprise in rural and urban area. Rural areas development is inevitable for the development of developing country like India. PMEGP provides high rate subsidies for setting up micro enterprises in rural areas. At national level Khadi and Village Industries Commission acted as nodal agency, at state level PMEGP implemented through Khadi and Village Industries Board and District Industries Center. In India PMEGP generates employment opportunities approximately 1,58,230 as on 23rd January,2015.So it is significant to study the role of Prime Minister's Employment Generation Programme in Kerala.

Key words: Industrialisation, Prime Minister's Employment Generation Program and Micro enterprise

1.INTRODUCTION

The employment generation in any country based on the level of development. So, when a country makes progress and it's production level becomes high, the employment opportunities increase (Gupta 2014). Industrialisation is one of the solutions for economic growth and employment generation. Govt of India introduced various employment generation programs with a view to eradicate poverty and for ensuring rural development. Prime Minister's Employment Generation Program (PMEGP) is one of the flagship program implemented by the Govt of India through the Ministry of Micro Small and Medium Enterprises. Prime Minister's Employment Generation Programme (PMEGP) is playing a vital role in promoting self-employment opportunities through micro and small industrial development by encouraging new entrepreneurs (Sanjeeb & RikoMihu, 2018).PMEGP is a credit linked capital subsidy scheme introduced to generate employment opportunities. PMEGP implemented through Kadhi and Village Industries Commission at national level, at state level Kadhi and Village Industries board and District Industries Centers. Prime Minister's Employment Generation Programme approximately generated over 11,13,000 employments during the last three years i.e. 2015-16 to 2017-18.Govt of Kerala also implemented PMEGP to generate employment opportunities.

2. LITERATURE REVIEW

(Deepakkuma & Kh.Dhiren, 2012)conducted a study on "Performance of PMEGP in Manipur" Performance measured on the basis of both primary and secondary data. The researcher observed that DIC sponsored 490 projects, 251 projects sponsored by Kadhi and Village Industries Board and state Kadhi and Village Industries Commission sponsered 238 projects during the year 2009-12.The study concluded that the product produced by KVI in the state has sufficient demand but supply not enough to meet the requirement. So it is necessary to diversify the KVI projects in to industries like Handmade Paper & Fibre and Polymer &Chemical industries with innovation and also ensure the effective utilisation of the rawmaterial available in the state.

(**Sharma 2014**)performed a study on "performance of Mizoram Kadhi and Village Industries Board under PMEGP scheme". The researcher analysed the pattern of financial assistance and performance of PMEGP and also studied the sales turnover of Kadhi and Village Industries board in Mizoram. The study revealed that during the study period Kadhi and Village Industries Board provide assistance to 1137 enterprises. It showed a continuous increase in number of unit financing. The study concluded that the Mizoram Kadhi and Village Industries Board played an active role in the economic development of the state.

(**Gupta 2014**)conducted a study on "Poverty alleviation programmes and employment generation in India Since 1991".The researcher mainly focused to study and analyse the poverty alleviation program, analyse impact of poverty alleviation program on rural employment generation and evaluate the relation between fund allocation and employment generation relating to each program. The researcher suggested that non Government organisation take part in the implementation of poverty alleviation program, ensure timely release of fund for the successful implementation of the programs and proper awareness programs arranged to familiarise poverty alleviation programs among the public

(Sanjeeb & RikoMihu, 2018)made a study on "impact of PMEGP on entrepreneurial development of tribal beneficiaries – A case study of lohit district of Arunachal Pradesh" .The researcher focused to analyse the impact of PMEGP in developing the entrepreneurship and socio-economic growth of the beneficiaries.The study observed that PMEGP had positive impact on entrepreneurial growth.The researcher concluded that PMEGP helped to solve the problem of operational and seed capital to some extent.

(**Dinesh, 2018**)made a study on "Prime Minister's Employment Generation Programme in Sikkim". The study mainly focused to analyse the performance of PMEGP in Sikkim,employment generated and identify the important problem problem related to entrepreneurial activity. The study revealed that the scheme helps to increase the income of rural people and to some extent it resolve the problem of unemployment among the youth.

3 OBJECTIVES OF THE STUDY

1. To study the conceptual framework of Prime Minister's Employment Generation Programme in India.
2. To compare the performance of Prime Minister's Employment Generation Programme in Kerala with India.

4. METHODOLOGY

4.1 Type of research: An analytical research design was adopted in this study.
4.2 Area of study: Study analyse and compare the performance of Prime Minister's Employment Generation Programme in Kerala state.
4.3 Source of Data: The present study is based on secondary data. The main source of data includes economic review 2016-2017, journals, Official web site of Ministry of MSME etc.

4.4 Statistical tools used: The information gathered was tabulated and analyzed by using percentage.

5 LIMITATIONS OF THE STUDY

Present study purely based on secondary data. Secondary data available only up to 2016-2017.

6 PRIME MINISTER'S EMPLOYMENT GENERATION PROGRAM

Prime Minister's Employment Generation Programme (PMEGP) was announced on 15th August, 2008 and launched in 2008-09. PMEGP is a credit-linked subsidy programme launched by Ministry of Micro Small and Medium Enterprises (MSME) for creation of employment opportunities through setting up micro enterprises in both rural and urban areas of the country. Micro enterprises are increasingly being viewed as a means for enhancing the income earning capacities of the youth (Gupta 2014).Prime Minister's Employment Generation Programme is a credit linked capital subsidy scheme introduced by Govt of India by merging existing two schemes namely Prime Ministers Rojgar Yojana(PMRY) and Rural Employment Generation Program(REGP) to create employment opportunities through the establishment of micro enterprises in rural and urban areas. (Ministry of MSME 2018).At national level the Scheme is implemented by Khadi and Village Industries Commission (KVIC). At the State level, the Scheme is implemented through State KVIC Directorates, State Khadi and Village Industries Boards (KVIBs) and District Industries Centres (DICs) and banks. The Government subsidy under the Scheme is routed by KVIC through the identified Banks for eventual distribution to the beneficiaries/entrepreneurs in their Bank accounts. The maximum cost of the project/unit admissible under manufacturing sector is Rs.25 lakh and under business/service sector is Rs.10 lakh. Any individual above 18 years of age at least VIII standard pass for projects costing above Rs.10 lakh in the manufacturing sector and above Rs. 5 lakh in the business/service sector eligible to apply. Only new projects are considered for sanction under PMEGP. Self Help Groups (including those belonging to BPL provided that they have not availed benefits under any other Scheme), Institutions registered under Societies Registration Act,1860; Production Co-operative Societies, and Charitable Trusts are also eligible. Existing Units (under PMRY, REGP or any other scheme of Government of India or State Government) and the units that have already availed Government Subsidy under any other scheme of Government of India or State Government are NOT eligible. (Ministry of MSME 2018)

OBJECTIVES OF PRIME MINISTERS EMPLOYMENT GENERATION PROGRAM

i. To generate employment opportunities in rural as well as urban areas of the country through setting up of new self-employment ventures/projects/micro enterprises.

ii. To bring together widely dispersed traditional artisans/ rural and urban unemployed youth and give them self-employment opportunities to the extent possible, at their place

iii. To provide continuous and sustainable employment to a large segment of traditional and prospective artisans and rural and urban unemployed youth in the country. (iv) To increase the wage earning capacity of artisans and contribute to increase in the growth rate of rural and urban employment. (Ministry of MSME 2018)

1.6.1 QUANTUM AND NATURE OF FINANCIAL ASSISTANCE: -

1 The maximum cost of project/unit admissible under manufacturing sector is Rs.25 lakhs.

2. The maximum cost of project/unit admissible under business / service sector is Rs.10 lakhs.

3. General category beneficiaries can avail of margin money subsidy of 25 % of the project cost in rural areas and 15% in urban areas. For beneficiaries belonging to special categories such as scheduled caste/scheduled tribe /women the margin money subsidy is 35% in rural areas and 25% in urban areas. (Ministry of MSME 2018)

Categories of beneficiaries under PMEGP	**Beneficiary's contribution (of project cost)**	**Rate of Subsidy (of project cost)**		**Term loan**
Area (location of project / unit)		**Urban**	**Rural**	The balance amount of the total project cost will be provided by Banks as term loan.
General Category	10%	15%	25%	
Special (including SC/ST etc.)	05%	25%	35%	

(Ministry of MSME, 2018)

7. IMPLEMENTING AGENCIES

The Scheme will be implemented by Khadi and Village Industries Commission (KVIC), Mumbai, a statutory body created by the Khadi and Village Industries Commission Act, 1956,which will be the single nodal agency at the national level. At the State level, the scheme will be implemented through State Directorates of KVIC, State Khadi and Village Industries Boards (KVIBs) and District Industries Centres in rural areas. In urban areas, the Scheme will be implemented by the State District Industries Centres (DICs) only. KVIC will coordinate with State KVIBs/State DICs and monitor performance in rural and urban areas. (Khadi and Village Industries Commission, 2018)

8. PERFORMANCE OF PMEGP IN KERALA

Kerala God's the own country, located on the southernmost tip of India. Kerala blessed with natural resources and also rich in educating youth. Govt of Kerala cannot able to meet the employment requirement of educated youth of the state. Industrialisation is one of the best possible ways to eradicate the problem of unemployment and also ensure the effective utilisation of available resources in the State. By considering these facts Prime Minister's Employment Generation Programme played an important role in generating employment opportunities and ensures a way for industrialisation. Central Govt. Flagship program PMEGP implemented by the state through Khadi and Village Industries Commission, Khadi and Village Industries Board and Directorate of industries and commerce. During the year 2015-2016 the number of units set up in Kerala 1, 36, 99,653 employment opportunities generated under this scheme. District Industries Center is leading in number of units set in Kerala under the scheme of PMEGP.DIC set up 734 units in Kerala under PMEGP during 2015-2016.

Table 1 Approximate Number of units set up in Kerala Under PMEGP -2015-2016

Sl No	**District**	**KVIC**	**KVIB**	**DIC**	**Total**
1	Thiruvananthapuram	33	8	78	119
2	Kollam	12	27	50	89
3	Pathanamthitta	9	27	75	111
4	Alappuzha	15	24	66	105
5	Kottayam	16	30	56	102

6	Idukki	30	13	37	80
7	Ernakulam	26	22	42	90
8	Thrissur	17	26	37	80
9	Palakkad	26	22	43	91
10	Malappuram	23	32	43	98
11	Kozhikode	12	28	73	113
12	Wayanad	32	20	40	92
13	Kannur	26	31	67	124
14	Kasargod	19	29	27	75
Total		**296**	**339**	**734**	**1369**

Source: Kadhi and Village Industries Commission

DISTRICT WISE PERFORMANCE OF PMEGP IN KERALA

Table 2 District wise Progress Report of PMEGP during 2016-17

Sl.No	District	Target in Lakh	No. of applications received	No. of applications selected by DTFCs	Margin Money involved (in Lakh)	No. of applications forwarded to banks	No. of applications sanctioned by banks	Margin Money sanctioned and released Lakh)	No. of persons given EDP training
1	2	3	4	5	6	7	8	9	10
1	Thiruvananthapuram	80.76	158	131	215.44	120	61	69.19	53
2	Kollam	80.76	120	101	23.6	101	60	101.07	44
3	Pathanamthitta	80.76	124	97	145.44	97	47	55.74	43
4	Alappuzha	70	142	141	335.07	141	61	95.52	44
5	Kottayam	68.42	144	133		130	48	67.35	48
6	Idukki	80.76	153	134	162.54	134	77	59.15	64
7	Ernakulam	80.76	249	197	277.81	197	86	75.27	60
8	Thrissur	80.76	158	116	187.52	116	58	39.83	110
9	Palakkad	85	136	110	178.08	110	58	94.09	66
10	Malappuram	80.76	92	67	121	67	49	112.69	36
11	Kozhikode	80.76	111	80	167.31	77	47	73.19	45
12	Wayanad	80.76	158	157	215.78	157	65	70	48
13	Kannur	70	81	70	91.21	70	40	40.8	25
14	Kasargod	80.76	92	57	101.72	57	26	37.99	19
	TOTAL	1101.02	1918	1591	2222.52	1574	783	991.88	705

Source: Directorate of Industries & Commerce

9.FINDINGS OF THE STUDY

The present study observed the following points.

1. In Kerala margin money utilised in 2015-2016 was 2720.48 lakhs. Margin money utilisation in Kerala shows an increasing trend by 1.54 percent.
2. In Kerala project set up under this scheme in 2015-2016 was 1369.Project set up under PMEGP in Kerala showed a 1.83 percent increase.
3. In Kerala employment generated under this scheme in 2015 was 9653.Employment generation under PMEGP in

Kerala showed 0.87 percent decrease as compared to previous year.

PMEGP generates employment opportunities approximately 1,58,230 as on 23rd January, 2015 in all over the country. More employment opportunities can be created by popularising the program through media and by way of simplifying the formalities.

CONCLUSION

Prime Minister Employment Generation Program implemented by the Govt with a view to create employment opportunities by setting up micro enterprise in rural and urban areas. Development of the rural area is essential for the development of a nation. So this program gave priority for the development of rural area also. PMEGP generates employment opportunities approximately 1,58,230 as on 23rd January, 2015 in all over the country .This shows that the performance of PMEGP in India is satisfactory. Performance of Kerala under this scheme showed an increasing trend in margin money utilisation and number of unit set up. But the employment generation showed a slight reduction. But as compared to India the performance of PMEG in Kerala is good. The study concluded that the effort of central Govt to generate employment opportunities through setting up micro enterprise is successful and it also ensures the development of rural area. So Employment generation through industrialisation is a possible solution.

REFERENCES

- Bhaskaran, E. (2011, August). The performance of Prime Minister's Employment Generation Programmein India. Retrieved from https://www.researchgate.net/publication/234016206_The_Performance_of_Prime_Minister_Employment_Generation_Programme_in_India
- Business standard. (2018, December). *Business standard.* Retrieved from Web site of business standard: https://www.business-standard.com/article/pf/citibank-launches-home-loan-product-linked-to-an-external-benchmark-118030700478_1.html
- D. G. (2018). Prime Minister Employment Generation Program in Sikkim-An analysis. *International Journal of research in social science* , 283-295.
- Deepakkuma, O., & K. M. (2012). Performance of PMEGP In Manipur. *Shiv Shakti International Journal in Multidisciplinary and Academic Research , 1*, 1-10.
- Gupta, Y. (2014). *Poverty alleviation programmes and employment generation in India Since 1991.* New Delhi: Shodhganga.
- Khadi and Village Industries Commission. (2018, December). *Khadi and Village Industries Commission.* Retrieved from Website of Khadi and Village Industries Commission: http://www.kvic.org.in/kvicres/update/pmegp/New%20PMEGP%20guidelines.pdf
- M.Usha. (2012). *Study on Rural Micro entrepreneurship under PMEGP in Guntur district of Andhra Pradesh.* Hyderabad: ACHARYA N. G. RANGA AGRICULTURAL UNIVERSITY.

- Ministry of MSME. (2018, December). *Ministry of MSME website*. Retrieved from https://msme.gov.in/11-prime-ministers-employment-generation-programme-pmegp
- Ministry of MSME. (2018). *My MSME*. Retrieved December saturday, 2018, from https://my.msme.gov.in/mymsme/reg/COM_PMEGPForm.aspx
- P. K., & Koley, a. (2015). Review of prime Ministers Employment Generation in the state of West Bengal. *International journal of business and administration review* , 139-147.
- S. K., & RikoMihu. (2018). Impact of PMEGP on entrepreneurial development of tribal beneficiaries-A case study of lohith District Arunachal Pradesh. *International Journal of recent scientific research* , 26321-26329.
- Sharma, L. S. (2014). An Analysis of the Performance of Mizoram Khadi and Village Industry Board under PMEGP Scheme. *European Academic research* , 2 (8), 10408-10417.
- Taneja, R. (2018, December). *Merinews.* Retrieved from Website of Merinews: http://www.merinews.com/mobile/article/India/2015/0/30/performance-under-pmegp-improves-at-national-level-msme-ministry/15903896

RECENT DEVELOPMENTS
IN
COMMERCE AND MANAGEMENT

EDITORS
Dr .P. VASANTHAKUMARI
Mrs. DEEPA.C
Mrs. SWAPNA.K

P.G DEPARTMENT OF COMMERCE
N.S.S COLLEGE, OTTAPALAM

English
RECENT DEVELOPMENTS IN COMMERCE AND MANAGEMENT
(Studies)

Editor : ***Dr .P. VASANTHAKUMARI***

First Published : June 2020
Cover Design : Book Media, Pala
Layout : Amrutha Syam
Printing : Book Media

Publishing

P.G Department of Commerce
N.S.S College, Ottapalam

Distribution

BOOK MEDIA
Pala - 686 575
Kottayam, Kerala, India.
Mobile +91 94475 36240
ISBN: 978-81-945634-02

Editorial

The growing Phenomenon of globalization, liberalization and Privatization has been immensely influencing the commerce and management field. Within the last decade, a lot of new trends have emerged in commerce and management field with a profound influence. The broad aim of this international conference was to explore and provide a platform of debate about global and nationwide developments in commerce and management. The seminar submissions in the form of paper on different aspects on the scheme after review process have been enclosed in this edited book.

We extend our profound thanks to the Management, The Principal, State bank of India, Regional branch, Shornur and resource persons who contributed greatly to this conference .We sincerely congratulate and thank all the authors for contributing their creative research work to this conference. We are also grateful to Book media who have helped to publish this edited Book.

Dr.P. Vasanthakumari
Head of the Department of commerce
N.S.SCollege, Ottapalam

INITIATIVE OFGOVERNMENT OF INDIA IN RURAL HOUSING

Sajeesh T J
Assistant professor,
Dept.of Commerce
S.E.S College,Sreekandapuram

Dr.Swarupa R
Associate Professor and
Research Guide
M.G College ,Iritty

Abstract

Shelter is the biggest dream and a requirement of everybody's life. It is a primary need along with food and clothes. A good home gives meaning and extent of his life. Adequate shelter for each and every household is a fundamental prerequisite for a healthy living in any society. The Government of India is considered to be of immense significance to shelter and all governments have highlighted its importance in their plans and policies. Pradhan Mantri Awas Yoajana is one of the important program implemented by the central Govt with a view to achieve the target to buit 2 crore houses across the nation's length and breadth.Estimated completion of the scheme is 2022.That means 2 crore houses will be constructed over a period of 7 years.It is significant to study the effect of Pradhan Mantri Awas Yoajana in reduction of rural housing shortage in rural area.

Key words: Housing shortage,Pradhan Mantri Awas Yojana,IndhiraawasYojana,Rural development

1.INTRODUCTION

Rural Development is essential for the Socio-Economic Development of the nation. The objective of rural development is to enrich the quality of human life in the rural areas (Gaikwad and Varade 2018).India suffered numerous problems. Housing is one of the major problem in India (M. and Vezhavethan 2018).The Government of India plays a coordinating and monitoring role and also supports the States/UTs through Centrally Sponsored schemes and programmes to overcome the housing problems.Govt of India implemented various program to reduce housing shortage in India.Pradhan Mantri Awas Yoajana is one of the important program implemented by the central Govt with a view to achieve the target to built 2 crore houses across the nation's length and breadth.Estimated completion of the scheme is 2022.That means 2 crore houses will be constructed over a period of 7 years. (Ministry of Rural Development Govt of India 2018)

2. LITERATURE REVIEW

Shelly (2017)studied "The role of the Pradhan Mantri Awas Yojana (urban), 2015 in financial inclusion in india".The reaesrcher mainly focused to study the conceptual framework of Pradhan Mantri Awas Yojana (urban) and assess the role of the Pradhan Mantri Awas Yojana (urban) in financial inclusion in India.The study observed that Pradhan Mantri Awas played a major role in urban financial inclusion.

Gaikwad and Varade (2018)conducted a study on "Pradhan Mantri Awaas Yojana–(gramin):"a step towards housing for all".The study examined the conceptual framework of Pradhan Mantri Awaas Yojana–(Gramin), assessed the role of Pradhan Mantri Awaas Yojana–(Gramin) in the villages of Union Territory of Dadra and Nagar Haveli, analyse the financial and physical achievements of Pradhan Mantri Awaas Yojana-Grameen and its implication in the villages of Union Territory of Dadra and Nagar Haveli.The study observed that villages of Union Territory of Dadra and Nagar Haveli effectively utilise the scheme and suggested that arrange more awareness program among rural people to popularise the scheme.

National institute of public finance and policy (2018)made a study on Impact of "Pradham Mantri Awaas Yojana Gr. min in income and employment".The researcher has been made an attempt to estimate the impact of PMAY-G in generating additional employment and income since 2016-17. The impact of the scheme on employment and income could be direct as well as indirect. The estimation is done under two stages. In the case of direct effect, the study uses PAHAL designs provided at the State level.

M. and Vezhavethan (2018)made a study on "A study on the housing in rural areas with special reference to pradhanmantriawasyojana (pmay-g)"The study focused to analyse the housing development in rural areas and also assess the implementation process of Pradhan Mantri Awas Yojana.The study observed that houses are well developed in rural areas under this scheme,thescheme is implemented properly in India and the target that was set by the government the implementation of this scheme clearly showed that there is remarkable increase in the housing project.

3.OBJECTIVES OF THE STUDY

1. To study the conceptual frame work of Pradhan Mantri Awas Yojana – Graminin India
2. To study the performance of Pradhan Mantri Awas Yojana –Graminin India.
3. To know the various housing schemes of Government of India.

4.METHODOLOGY

4.1 TYPE OF RESEARCH

This research is based on a analytical and descriptive research methodology.

4.2 AREA OF STUDY

The study focus on the India as a whole and special reference to urbanization of India.

4.3 SOURCE OF DATA

The present study based on secondary data. The main source of data includes, journals, official website of census India etc.

5 HISTORY OF RURAL HOUSING PROGRAM IN INDIA

In our country public housing program started with the rehabilitation of refugees immediately after independence. Till the year 1960, approximately 5 lakh families were provided housing in different parts of India. In 1957, as a part of the community development movement a village housing program was introduced providing loans to individuals and cooperatives upto Rs.5000/- per unit. Only 67,000 houses could be constructed in this scheme till the end of 5 year plan.

Specific focus on rural housing in India,has its origin in the wage employment program of National Rural Employment Program(NREP-1980) and Rural Landless Employment Guarantee Program (RLEGP-1983)by allowing construction of houses under these program for SCs/STs and freed bounded labourers.Afull fledged rural housing program Indira Awaas Yojana(IAY) was later launched in June 1985 as a sub scheme of RLEGP.WhenJawaharRozgat Yojana was launched in April 1989, 6 percent of fund were allocated to housing for SCs/STs and freed bonded labourers.In 1993-94,the coverage was extended to Non-SC/ST families by increasing the earmarked fund for housing under JRY to 10 persent.The additional 4 percent was to be used for non SC/ST category of beneficiaries.

Indira Always Yojana (IAY) was made an independent program with effect from 1st January 1996 aimed at addressing the housing needs of the below Poverty Line (BPL) households. After more than 30 years of its implementation, although LAY addressed the rural housing shortage considerably, however in view of the limited scope of coverage under the program there still are considerate gaps in rural housing.

Government has committed to provide "Housing for All" by 2022.To fulfil the Government's commitment and to address rural housing gaps. IAY has been restructured into Pradhan Mantri Awas Yojana-Gramin (PMAY-G) with effect from April 2016. (Ministry of Rural Development Govt of India 2018)

6. PRADHAN MANTRI AWAS YOJANA – GRAMIN

The Pradhan Mantri Awas Yojana (PMAY) Credit Linked Subsidy Scheme (CLSS) - scheme launched by our honourable Prime Minister ShriNarendra 'Housing for All' is a home loan.The PMAY scheme for the people who belong to lower income group,economically weaker section and middle income group in India.The scheme envisions 'Housing for All' by the year 2022 (Pradhan Mantri Yojana 2018).The scheme devided into two parts PMAY Urban and PMAY Gramin.PMAY urban house will be constructed with in urban areas.PMAYGramin scheme introduced for peole in rural areas.People who are living in rural areas in rented houses or own houses but need construction eligible to apply PMAY Gramin.PMAY launched on June 2015.The main objective of this program is to ensure that 2 crore houses are built across the nation's length and breadth.Estimated completion of the scheme is 2022.That means 2 crore houses will be constructed over a period of 7 years. (Pradhan Mantri Yojana 2018)

"Housing for All" Mission for urban area has been implemented with effect from 17.06.2015 to provide central assistance to implementing agencies. The Credit Linked Subsidy Scheme is being offered under this mission.For Middle Income Group(MIG), the interest subsidy will be provided on housing loans for acquisition/construction of houses (including repurchase).For Economically Weaker Section(EWS)/Lower Income Group(LIG), the interest subsidy will be provided on housing loans for acquisition, construction of house. The Credit Linked subsidy would also be available for housing loans availed for new construction and addition of rooms, kitchen, toilet etc. to existing dwellings as incremental housing.The interest subsidy benefit will be upfront on the principal outstanding.

The availability and amount of interest subsidy is subject to meeting income criteria as per various category under this scheme. (Ministry of Rural Development Govt of India 2018)

Table:1 Pradhan Mantri Awas Yojana Scheme Grid

Annual Household Income (Rs.)	Categories	Interest Subsidy (%)	Subsidy Calculated on Max. Loan of (Rs.)	Max. Interest Subsidy of	Max. Carpet Area of the Property
Upto 3 lakh	EWS	6.50%	6,00,000	2.67 lakh	No Limit **
3 lakh	LIG	6.50%	6,00,000	2.67	No

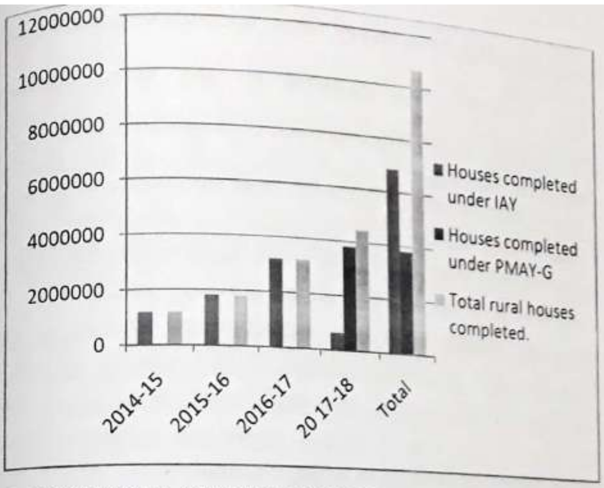
to 6 lakh				lakh	Limit **
6 lak to 12 lakh	MIG-1	4.00%	9,00,000	2.35 lakh	1291 sq. ft.
12 lakh to 18 lakh	MIG-2	3.00%	12,00,000	2.30 lakh	1614 sq. ft

TABLE.2 HOUSES CONSTRUCTED UNDER PMAY

Financial year	Houses completed under IAY	Houses completed under PMAY-G	Total rural houses completed
2014-15	1193000	0	1193000
2015-16	1823000	0	1823000
2016-17	3212000	2000	3214000
20 17-18	636000	3818000	4454000
Total	6864000	3820000	10684000

Source:

A total of 1.07 crore rural houses have been completed over the last four years (2014-15 to 2017-18) which include completion of 38.20 lakh Pradhan Mantri Awaas Yojana – Gramin (PMAY- G) houses and 68.64 lakh IAY houses that were sanctioned in 2014-15 and 2015-16 and prior to that. If the figures of the current financial year are also added to this achievement under the rural housing scheme the achievement from 2014-15 till date becomes 1.13 crore completed rural houses. A summary of houses completed, as on 31.7.2018, which shows an upward swing, is shown below:



7. FINDINGS OF THE STUDY

The increasing population and urabnisation resulted in Indian housing shortages; the housing shortage in India has touched 18.78 million units. All the governments have provided with great importance to housing in their plans and policies. Government has acknowledged the importance of the housing issues in the country in the current five-year plans. Under PMAY, it is proposed to build 2 crore houses for urban poor including Economically Weaker Sections and Low Income Groups in urban areas by the year 2022 through a financial assistance of 2 trillion from central government.

In India as a part of Indhiraawas Yojana and Pradhan Mantri Awaas Yojana – Graminrural houses completed a total of 1.07 crore over the last four years (2014-15 to 2017-18) .It includes completion of 38.20 lakh Pradhan Mantri Awaas Yojana – Gramin (PMAY- G) houses and 68.64 lakh IAY houses that were sanctioned in 2014-15 and 2015-16 and prior to that.

CONCLUSION

Rural development is essential for the socio economic development of India.Rural development is possible by way of improving the standard of living of the people in rural area.Food,shelter and cloth are the basic necessities of a human being.Pradhan Mantri Awas Yojana is help to achieve the goal house for all. A total of 1.07 crore rural houses have been completed over the last four years (2014-15 to 2017-18) this shows an upward trend in construction of housing in rural areas.The main hindrance relating to this scheme is lack of awareness among the rural people about Pradhan Mantri Awas Yojana.With the help of proper awareness program through media reduce the hindrances to some extend.

REFERENCES

- Bajaj Finserv. *Bajaj Finserv.* December 2018. https://www.bajajfinserv.in/home-loan-pradhan-mantri-awas-yojana.
- Gaikwad Arun Hari, and Chetan S. Varade. "Pradhan Mantri Awas Yojana-Gramin"a step towards housing for all"." *nspira-Journal of Modern Management & Entrepreneurship (JMME)*, 2018: 335-339.
- M. Swathi, and D. Vezhavethan. "Study on the housing in rural areas with special reference to Pradhan Mantri Awas Yojana-Gramin." *International journal of pure and applied mathematics*, 2018: 87-99.
- Ministry of Rural Development Govt of India. *Web site of Ministry of Rural Development Govt of India* . December 2018. https://pmayg.nic.in/netiay/Uploaded/English_Book_Final.pdf.

- National institute of public finance and policy. *Web site of National institute of public finance and policy.* December 2018. https://rural.nic.in/sites/default/files/IMPACT_OF_PMAY-G_ON_INCOME_AND_EMPLOYMENT_REPORT.pdf.
- Pradhan Mantri Yojana. *Pradhan Mantri Yojana.* Decenber 2018. https://www.pradhanmantriyojana.co.in/pm-awas-yojana/.
- Shelly De. "The role of Pradhan Mantri Awas Yojana Urban-2015 in financial inclusion in India." *International Journal of recent scientific research*, 2017: 18959-18962.